Submitted to Journal of the American
Chemical Society

LBL-3470
Preprint c.2

ELECTRONIC STRUCTURE OF DICARBONYLS: THE GROUND STATE OF GLYOXAL

Clifford E. Dykstra and Henry F. Schaefer III

March 1975

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-3470 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-3470

Electronic Structure of Dicarbonyls: The Ground State of Glyoxal*

Clifford E. Dykstra** and Henry F. Schaefer III***

Department of Chemistry and Lawrence Berkeley Laboratory

University of California, Berkeley, California 94720

* Work performed under the auspices of the U.S. Energy Research and Development Administration.

** Du Pont Graduate Fellow.

*** Alfred P. Sloan Fellow, 1972-1974.

INTRODUCTION

The reactivity, photochemistry, photophysics and other properties of carbonyl containing molecules have made them the subject of a wide variety of experimental studies. It is clear that such properties are intrinsically related to molecular electronic structure. Of particular interest in large or complex systems is determining the effect of localized CO electronic structure so as to facilitate prediction of the chemistry or properties of such systems. With existing theoretical descriptions of the electronic structures of simple carbonyl molecules, such as carbon monoxide[1-8] and formaldehyde,[9-16] a direct approach to this problem would be the theoretical study of a series of systems of more than one carbonyl. And an obvious beginning point is the simplest dicarbonyl, glyoxal.

Glyoxal has been an interesting molecule in photochemistry and spectroscopic studies since the early photolysis experiments of Norrish and Griffiths.[17] Their work and that of others[18-19] showed the dissociation products of glyoxal to be CO, formaldehyde and hydrogen molecules. While the production of formaldehyde involves excited electronic states,[20-21] it appears hydrogen is formed from vibrationally excited ground electronic state molecules.[22] Spectroscopic work has shown the structure of the major form of glyoxal to be planar trans.[23-24] In 1970, cis-glyoxal was identified by high resolution visible spectroscopy[25-26] and its planar structure was confirmed by microwave experiments.[27] No gauche forms have been detected.

The structure and properties of glyoxal depend largely on the valence molecular orbitals (MO's). Within the paradigm of carbonyl chemistry, these are expected to correlate with oxygen non-bonding orbitals and CO π orbitals. Since only a few excited states of glyoxal have been identified [23-24,26,28], photoelectron spectroscopy along with semi-empirical and ab initio calculations have been used to study the valence molecular orbitals. However, the results have not been entirely consistent.

Turner's assignment of the photoelectron spectrum of glyoxal[29] ordered the valence molecular orbitals as n_a, n_b, π_b and π_a in order of increasing ionization potential (a and b subscripts denote C_2 rotational symmetry). The spectra also indicated the level separations were of about the same magnitude. This seems in agreement with CNDO calculations[30] showing the $n_a - n_b$ splitting of otherwise degenerate non-interacting orbitals to be due to a through-bond interaction with the carbons. The acceptance of this description of the valence molecular orbitals has limited the search for excited states to $n \rightarrow \pi^*$ excitations, with the $\pi \rightarrow \pi^*$ states presumed to be much higher in energy. Qualitative interpretations concerning the O-C-C-O skeleton of biacetyl[31] and CNDO/CI calculations[32-33] of α-dicarbonyls have given generally the same ordering with some differences in the $n_a - n_b$ separation. Also, minimum basis ab initio calculations[34] on the negative ion, $(CHO)_2^-$, have agreed with this ordering, though with some σ MO's located energetically among the n and π MO's.

The first work inconsistent with this MO scheme was the semi-empirical study of Kato *et al.*[35] They found the valence molecular orbitals to be ordered n_a, π_b, n_b, σ_a, π_a in the *trans* form and n_a, π_a, n_b, σ_a, π_b in the *cis* form. The separation of the highest π and lowest n for both forms tended to be smaller than the other level separations. The important implications of this was seen in their prediction that $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states would not be completely apart energetically. Pincelli *et al*[36] used a double-zeta basis in an *ab initio* calculation on the ground state. They found an ordering of valence MO's similar to that of Kato, but with the highest σ MO's being lower than the n and π MO's. And a more recent calculation[37] with a less than double-zeta basis seems to agree, assuming that the symmetry designations presented should be interchanged.

Ab initio calculations[36-39] have been limited to the ground state. All have sought to determine the internal rotation barrier and the *cis-trans* separation, but the results have disagreed by as much as a factor of two. This may be due to both the use of different basis sets and to different treatments of the geometry. Only one of these calculations[39] involved optimization of the geometry, which Dunning and Winter have demonstrated to be potentially important in internal rotation problems.[40]

The persistent electronic structure problem, then, is the determination of the nature of the highest filled molecular orbitals. A careful study of the ground state of glyoxal, including the internal rotation potential, and comparison with the interaction

of two CO molecules may resolve this problem and improve understanding of dicarbonyl excited states.

THEORETICAL APPROACH

A double-zeta basis set of Dunning-contracted gaussian functions[41] was used in all calculations:

C	(9s5p/4s2p)
O	(9s5p/4s2p)
H	(4s/2s)

The quality of this basis set in LCAO-MO-SCF calculations has been reviewed elsewhere.[42]

The five independent structural parameters in glyoxal are the carbon-carbon, carbon-oxygen and carbon-hydrogen bond distances, and the carbon-carbon-oxygen and carbon-carbon-hydrogen bond angles. The gas-phase electron diffraction values of these parameters[43] for trans-glyoxal were used as a guess of the SCF optimum geometry. The parameters were varied iteratively and a simple parabolic fit of the molecular energy was used to predict the minimum with respect to the given parameter. The size of the variations was reduced after one cycle through all the parameters, and the process continued until the change in both the parameters and the energy became reasonably small. In all cases, the internal rotation angle, ϕ, was held fixed. Tests were made with other starting geometries to insure that the iterative method had not converged to a local minimum. The optimization was performed for the trans ($\phi = 0°$), cis ($\phi = 180°$), and three gauche forms: $\phi = 45°, 90°, 135°$.

The symmetry representations of the molecular orbitals were an obviously important consideration. Glyoxal is a 30-electron system with a closed shell ground state. The molecular symmetry is C_{2h} in trans, C_{2v} in cis and C_2 for the gauche forms. The three forms are illustrated in Figure 1. It can be seen that the C_2 rotation axis is in the molecular plane of the cis form, but perpendicular to the trans molecular plane. To check previous determinations of the orbital occupancies, SCF calculations were first performed in the reduced symmetry, C_2, on the cis and trans forms. The resulting molecular orbitals could then be identified with full symmetry representations.

As shown in Figure 2, oxygen non-bonding 2p atomic orbitals are combined symmetrically and antisymmetrically in order to transform as point group representations. This yields a_g and b_u in trans and a_1 and b_2 in cis, and like σ MO's they are clearly in the molecular plane. The π MO's are formed from atomic p orbitals perpendicular to the molecular plane and thus transform as a_u and b_g in trans and a_2 and b_1 in cis. The n and π descriptions are not appropriate in the reduced symmetry of the gauche structures. Since no p functions were used in the hydrogen basis, the π MO's are completely localized on the O-C-C-O skeleton and correlate directly with individual carbon monoxide MO's.

RESULTS AND DISCUSSION

The double-zeta basis set and geometry optimization yielded an energy for trans-glyoxal lower than any previous calculation, as shown in Table I. The structural parameters for the optimized geometries are given in Table II. While all the changes were small, an increase in the C-C bond length and a decrease in the C-O bond length in going from trans to cis were found. Also, the C-C-O bond angle was found to be about 2.1° larger in the cis form than in the trans. This compares with experimental values of about 2.7°[27] and 3°.[44] The C-H bond length was essentially the same in all structures.

The internal rotation barrier was calculated by a standard fit to a cosine series potential function and was found to be 7.5 kcal/mole at an internal rotation angle of 102°. The potential is shown in Figure 3. The energy difference between the cis and trans forms was 0.0094 hartrees or 5.9 kcal/mole. Both values are within the range of previous calculations. The major disagreement is with the calculation of Ha[37] who used a near double-zeta atomic basis with assumed geometries, and obtained only 3.0 kcal/mole for the cis-trans separation. Ha's result is probably due to a choice of geometry far from the optimum. Indeed, the energy obtained by Ha with the near-double-zeta basis is about as good as that of Pople and coworkers[38] who used a smaller 4-31G basis.

Sundberg and Cheung used a somewhat less than double-zeta basis and performed a partial geometry optimization.[39] Specifically for the gauche forms they did not optimize the carbon-hydrogen and carbon-oxygen bond lengths

and the carbon-carbon-hydrogen angle. While qualitatively they show a C-C bond length increase and a C-O bond length decrease, their C-C lengths are overall longer than determined in this work, and C-O lengths are shorter. Furthermore, their reported change between cis and trans in the CCO angle is smaller and less in line with experimental values.[27,44] A possible reason for these differences is that they used a larger set of primitives on oxygen than on carbon. Finally, though the change in the C-C-H bond angle is small, it is opposite in direction from our results. All of these geometry effects may be the result of their use of a less complete basis than our double-zeta set. The same considerations might explain their somewhat small cis-trans separation energy.

A double-zeta set was used by Pincelli and coworkers in an earlier calculation.[36] However, no geometry optimization was attempted, and we attribute part of the improvement in the total molecular energy over their result to the optimization. It seems that because the structural changes upon internal rotation are small, the barrier and separation results of the double-zeta calculation of Pincelli et al. are in qualitative agreement with the present work.

Experimental studies of the internal rotation potential have been limited. Currie and Ramsay used the difficult technique of following the temperature dependence of absorption intensity of vibrational bands in the visible absorption spectrum.[26] They reported the cis-trans energy difference to be 1125 cm^{-1} or 3.2

kcal/mole. More recently, Durig and coworkers presented an internal rotation potential with a barrier of about 4.6 kcal/mole,[27] but the determination of their potential explicity used the cis-trans

separation energy of Currie and Ramsay. Before the existence of cis-glyoxal was known, Fately and coworkers estimated a potential barrier of 13.7 kcal/mole using infrared frequencies of torsional vibrations in trans-glyoxal.[45] The inherent difficulties of both of the independent experimental approaches would suggest only that the true value may be somewhere between.

After completing the geometry optimization, the carbon-carbon stretching potential curve was studied. For both cis and trans glyoxal, seven C-C distances covering a range of 0.17 Å around the minima were selected and the molecular energy calculated at each point. All other parameters were fixed at their optimum values. In the region where the potential curves are harmonic, the ratio of the increases in energy above the respective minima (for equivalent displacements) is a measure of the ratio of the two force constants. This type of comparison gave about a 5% smaller value for the cis than trans form with the difference increasing at larger C-C distances as anharmonicity becomes more important. This confirms that the cis C-C potential is slightly shallower than the trans potential, a fact which could be physically significant. In 1964, Parmenter used quantum yield studies to show that vibrationally excited ground electronic state molecules could dissociate to produce hydrogen and carbon monoxide.[22]

$$(CHO)_2^* \rightarrow H_2 + 2\ CO$$

Parmenter estimated that $(CHO)_2^*$ must be formed with about 55 kcal/mole of internal energy in his experiments. Clearly, with a cis-trans

barrier of 7.5 kcal/mole, $(CHO)_2^*$ could easily interconvert between *cis* and *trans*. The comparison of the C-C potentials in the two forms suggests that breaking the C-C bond, which is necessary for the observed dissociation, should be at least as likely and perhaps more likely in the *cis* form. It is interesting to note, that if the dissociation is unimolecular, formation of H_2 would be favored in the *cis* form because the hydrogen atoms are spatially much closer.

For each of the five optimized glyoxal geometries, the dipole moment was calculated using the SCF wavefunctions, and the results are given in Table III. Symmetry requires the dipole moment of *trans*-glyoxal to be identically zero. The calculated value of 4.79 Debyes for the *cis* form agrees fortuitously well with the microwave spectroscopy value of 4.8 d.[27]

Details of Electronic Structure

The orbital energies of glyoxal and CO-CO reveal much about their electronic structure. The energies are given in Tables IV and V and are plotted in Figures 4 and 5. The first interesting feature is that the ordering of glyoxal MO's is n, π, n and π; or, more importantly, the π and n MO's are not completely separate energetically. Also, the π_a and π_b MO's while about 0.074 hartrees apart in both the *cis* and *trans* forms, reverse their order between the forms. And because only a and b symmetry is maintained in the *gauche* forms, the *trans* π_b necessarily correlates with the *cis* n_b. The *trans* n_b becomes the *cis* π_b.

The Mulliken populations given in Table VI demonstrate the atomic character of the valence MO's. The oxygen p atomic orbitals (AO's) form the n_b orbital almost exclusive of contributions from any other center. However, hydrogen and carbon do participate in the n_a MO. The *trans* π_b and *cis* π_a, which are the highest π's energetically, have a node between the carbons (see Figure 2). Thus, the oxygen p contribution to these MO's dominates the carbon p contribution. In the other π MO's, there is no node and the carbon p population is more nearly equivalent.

The MO's which result from the interaction of two CO molecules have some similarity to glyoxal MO's. As shown in Figure 5, the degeneracy of the σ and π MO's of the two separate carbon monoxide molecules is lost by the interaction at distances of about 7 bohrs

or less. In C_{2h} or C_{2v} symmetry, the oxygen p AO's directed along the C-O axis can mix with oxygen p AO's perpendicular to the axis but in the CO-CO plane. As a result, the individual highest filled σ MO's of CO correlate with n orbitals in CO-CO. The components of the carbon monoxide π MO's become π CO-CO MO's and σ-like low lying molecular orbitals.

In the trans arrangement, the highest orbitals at a carbon-carbon distance corresponding to the optimized glyoxal structure are qualitatively similar to trans-glyoxal. The difference is that the n_b rather than n_a orbital is highest energetically and, in fact, substantially higher than the n_a glyoxal orbital. Similarly, n_b is higher than n_a in the cis arrangement unlike cis-glyoxal. An additional observation is that while the $n_a - n_b$ separation is nearly the same in cis and trans-glyoxal, it is much larger in cis CO-CO than trans.

Understanding this unexpected reversal in the ordering of the oxygen n MO's requires a detailed examination of the orbitals. We first observe that in both CO-CO and glyoxal, the most non-interacting n orbital is strictly lowest in energy regardless of a or b symmetry. The remaining n orbital tends to be more delocalized over the whole molecule. Examining this orbital explains the $n_a - n_b$ ordering. In CO-CO, the oxygen p AO's in the anti-symmetric combination, n_b, interact with the carbon 2s AO's. But since the two carbon 2s AO's combine anti-symmetrically, the molecular orbital has significant carbon-carbon anti-bonding character. Hence, it is energetically higher than the non-interacting n_a. In glyoxal, the n-pair which

delocalizes has two additional hydrogen centers available. Thus, the interaction with the carbons is that which allows overlap with hydrogen AO's. Clearly, the best choice is carbon 2p AO's and, indeed, the Mulliken population analysis indicates the carbon participation in the n_a glyoxal orbital to be p rather than s. With this delocalization, the interacting carbon 2p AO's are roughly perpendicular to the C-C axis and have no anti-bonding character. With the most non-interacting pair being lowest in energy, n_b is lower than n_a in glyoxal.

To explain why the interaction in CO-CO is with carbon s AO's while in glyoxal it is with carbon p AO's, let us look at the total set of molecular orbitals. First, in CO-CO and glyoxal, the symmetric combination of carbon 2s gives a low-lying C-C σ bond which is unlikely to interact. Second, in CO-CO the carbon 2p orbitals participate in forming a C-C σ bond, a C-O π bond (out of plane) and a C-O σ bond. Only an antisymmetric combination of the p or s AO's which formed C-C σ orbitals is available for interaction with oxygen n electrons. The 2s is favored over the 2p and the n_b orbital interacts with the carbons. But in glyoxal, the carbon 2p AO's along the C-C axis, rather than forming a C-C σ orbital, can form a strong C-H σ bond along with the carbon 2s. With the electron density primarily in the C-H region and withdrawn from the C-C region, the symmetric or anti-symmetric combination of the C-H bonds into a molecular orbital should be equally likely. The Mulliken population analysis indicates this orbital has b symmetry. Therefore, the symmetric combinations now participate in the formation

of the C-O σ bonds leaving carbon 2p AO's perpendicular to the C-C axis available for interaction with oxygen n electrons.

Internal rotation of glyoxal provides another view of oxygen n interaction. As previously pointed out, the $n_a - n_b$ separation in orbital energies is about the same in cis and trans glyoxal. In the gauche forms, the n designation is inappropriate and no comparison is possible. Swenson and Hoffmann, using CNDO calculations, have concluded that the interaction which removes the n orbital degeneracy is a through-bond interaction with the carbons.[30] In a general sense, if the interaction were through-space instead of through-bond, then bringing the oxygens spatially closer should increase the $n_a - n_b$ separation. Since this separation does not increase when the oxygens are spatially closer in the cis form, our results support a through-bond interpretation. However, Swenson and Hoffmann believe that the interaction is with carbon p AO's directed along the C-C axis, whereas we find the interaction to be with carbon p AO's perpendicular to this axis. Furthermore, we feel that hydrogen is essential for the interaction, while Swenson and Hoffmann do not consider the effect of the hydrogens. Were their view precisely correct, the $n_a - n_b$ ordering in CO-CO should be the same as glyoxal. The present calculations suggest that this is not the case. Therefore, the degeneracy of the oxygen n orbitals may not be removed by a through-space interaction, but rather by an interaction dependent on the total molecular structure, not just the O-C-C-O skeleton.

Chemically, this understanding of the electronic structure of the model α-diketone, glyoxal, can lead to some generalizations.

For instance, substitution of an alkyl group for hydrogen, such as in biacetyl, should improve stability of the α-diketone. The interaction of the n_a orbital is expected to increase since delocalization of the electrons over the alkyl group would be greater than with hydrogen. This would stabilize or lower the energy of the n_a MO and the molecular stability would be enhanced. Thus, the $n_a - n_b$ separation in biacetyl should be smaller than in glyoxal.

An important consequence of the ordering of the n and π valence MO's in glyoxal is the nature of the low-lying excited states. As can be seen from Figure 4, the lowest excited states are probably excitations from the n_a orbital. However, in contrast to all but the semi-empirical calculations of Kato et al,[35] excitations from the highest π MO should also yield low-lying electronic states. This is a direct result of the n and π MO's not being completely energetically separate as often believed. In a preliminary calculation on the excited states of glyoxal, we have, in fact, found that $\pi \rightarrow \pi^*$ excited states are among the $n \rightarrow \pi^*$ states.

ACKNOWLEDGMENTS

The computations were carried out on the Datacraft 6024/4 minicomputer, supported by the National Science Foundation, Grant GP-39317.

REFERENCES

1. W. M. Huo, J. Chem. Phys. 43, 624 (1965).
2. R. K. Nesbet, J. Chem. Phys. 44, 4403 (1965).
3. M. Yoshimine and A. D. McLean, Intern. J. Quantum Chem. 1S, 313 (1967).
4. F. Grimaldi, A. Lecourt, and C. M. Moser, Intern. J. Quantum Chem. 1S, 153 (1967).
5. S. V. O'Neil and H. F. Schaefer, J. Chem. Phys. 53, 3994 (1970).
6. S. Green, J. Chem. Phys. 52, 3100 (1970).
7. A. K. Q. Siu and E. R. Davidson, Intern. J. Quantum Chem. 4, 223 (1970).
8. F. P. Billingsley and M. Krauss, J. Chem. Phys. 60, 4130 (1974).
9. J. M. Foster and S. F. Boys, Rev. Mod. Phys. 32, 303 (1960).
10. S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. 45, 3457 (1966).
11. T. H. Dunning, N. W. Winter, and V. McKoy, J. Chem. Phys. 49, 4128 (1969).
12. D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. 50, 2216 (1969).
13. W. H. Fink, J. Amer. Chem. Soc. 94, 1073, 1078 (1972).
14. S. R. Langhoff, S. T. Elbert and E. R. Davidson, Intern. J. Quantum Chem. 7, 999 (1973).
15. R. L. Jaffe, D. M. Hayes and K. Morokuma, J. Chem. Phys. 60, 5108 (1974).

16. B. J. Garrison, H. F. Schaefer, and W. A. Lester, J. Chem. Phys. 61, 3039 (1974).

17. R. G. W. Norrish and J. G. A. Griffiths, J. Chem. Soc. 1928, 2829.

18. F. E. Blacet and R. W. Moulton, J. Amer. Chem. Soc. 63, 868 (1941).

19. F. H. Dorman and A. S. Buchanan, Australian J. Chem. 9, 49 (1956).

20. J. T. Yardley, J. Chem. Phys. 56, 6192 (1972).

21. L. G. Anderson, C. S. Parmenter, and H. M. Poland, Chem. Physics 1, 401 (1973).

22. C. S. Parmenter, J. Chem. Phys. 41, 648 (1964).

23. J. C. D. Brand, Trans. Faraday Soc. 50, 431 (1954).

24. J. Paldus and D. A. Ramsay, Can. J. Phys. 45, 1389 (1967).

25. W. Holzer and D. A. Ramsay, Can. J. Phys. 48, 1759 (1970).

26. G. N. Currie and D. A. Ramsay, Can. J. Phys. 49, 317 (1971).

27. J. R. Durig, C. C. Tong, and Y. S. Li, J. Chem. Phys. 57, 4425 (1972).

28. J. Kelder, H. Cerfontain, J. K. Eweg, and R. P. H. Rettschnick, Chem. Phys. Letts. 26, 491 (1974).

29. D. W. Turner, Molecular Photoelectron Spectroscopy (Wiley-Interscience, 1970) p. 252.

30. J. R. Swenson and R. Hoffmann, Helv. Chim. Acta 53, 2331 (1970).

31. E. Drent and J. Kommandeur, Chem. Phys. Letts. 14, 321 (1972).

32. W. Hug, J. Kuhn, K. J. Siebold, H. Labhart, and G. Wagniere, Helv. Chim. Acta 54, 1451 (1971).

33. J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, J. Amer. Chem. Soc. 96, 4385 (1974).

34. D. C. McCain and D. W. Hayden, J. Mag. Resonance 12, 312 (1973).

35. H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, Bull. Chem. Soc. Japan 40, 2761 (1967).

36. U. Pincelli, B. Cadioli, and D. J. David, J. Mol. Structure 9, 173 (1971).

37. T. Ha, J. Mol. Structure 12, 171 (1972).

38. L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, Australian J. Chem. 25, 1601 (1972).

39. K. R. Sundberg and L. M. Cheung, Chem. Phys. Letts. 29, 93 (1974).

40. T. H. Dunning and N. W. Winter, Chem. Phys. Letts. 11, 194 (1971).

41. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

42. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Massachusetts, 1972).

43. M. Kuchitsu in Molecular Structure and Properties, G. Allen, Ed. (University Park Press, Baltimore, Maryland, 1972).

44. D. A. Ramsay and C. Zauli, Acta Physica Acadamia e Scientarum Hungaricae 35, 79 (1974).

45. W. G. Fately, R. K. Harris, F. A. Miller, and R. E. Witkowski, Spectrochimica Acta 21, 231 (1965).

TABLE I. Glyoxal ground state energies.

	Trans Energy	Cis / Trans Separation	Barrier
	hartrees	kcal/mole	kcal/mole
This work	-226.5182	5.9	7.5
Pincelli *et al*[a]	-226.4703	6.4	7.9
Sundberg *et al*[b]	-226.3246	4.8	7.2
Ha[c]	-226.2477	3.0	6.2
Radom *et al*[d]	-226.2428	6.1	7.9

[a] Ref. 36

[b] Ref. 39

[c] Ref. 37

[d] Ref. 38; barrier is taken from the $\phi = 120°$ potential.

TABLE II. Glyoxal geometry optimization. Bond distances are in Å, and bond angles in degrees.

	ϕ	R_{CC}	R_{CO}	R_{CH}	$\angle CCO$	$\angle CCH$	Energy[a] hartrees
trans	0°	1.508	1.215	1.085	121.1	116.0	0.0
	45°	1.509	1.215	1.085	121.4	116.0	0.0053
	90°	1.512	1.215	1.085	122.7	116.0	0.0116
	102°	Potential maximum[b]					0.0119
	135°	1.514	1.214	1.085	123.1	115.5	0.0107
cis	180°	1.516	1.213	1.085	123.2	115.3	0.0094

[a] Energy is relative to trans.

[b] Determined from potential curve.

TABLE III. Dipole moments (in Debyes).

	ϕ	μ
trans	0°	0.0
	45°	2.03
	90°	3.66
	135°	4.55
cis	180°	4.79
cis[a]		4.8

[a] Microwave experimental result, Ref. 27.

TABLE IV. Glyoxal orbital energies in hartrees. These are the highest occupied molecular orbitals in the ground state.

Trans			Gauche				Cis		
Molecular Orbital		$\varepsilon_{0°}$	Molecular Orbital	$\varepsilon_{45°}$	$\varepsilon_{90°}$	$\varepsilon_{135°}$	Molecular Orbital		$\varepsilon_{180°}$
$5\ b_u$	σ	-0.7076	5 b	-0.7025	-0.6890	-0.6717	$6\ a_1$	σ	-0.6802
$6\ a_g$	σ	-0.6580	6 a	-0.6665	-0.6735	-0.6779	$5\ b_2$	σ	-0.6593
$1\ a_u$	π_a	-0.6041	7 a	-0.5853	-0.5548	-0.5325	$1\ b_1$	π_b	-0.5981
$6\ b_u$	n_b	-0.5349	6 b	-0.5366	-0.5536	-0.5805	$6\ b_2$	n_b	-0.5253
$1\ b_g$	π_b	-0.5305	7 b	-0.5351	-0.5358	-0.5304	$1\ a_2$	π_a	-0.5239
$7\ a_g$	n_a	-0.4484	8 a	-0.4440	-0.4387	-0.4414	$7\ a_1$	n_a	-0.4456

TABLE V. CO-CO interaction and orbital Energies. Geometries were analagous to glyoxal optimized structures with only R_{C-C} being varied.[a] The carbon-carbon separation is in bohrs and energies are in hartrees.

	R_{C-C} =	R^b_{opt}	4.0	5.0	7.0	10.0	30.0
Cis	Energy	-225.1697	-225.3048	-225.3388	-225.3480	-225.3480	-225.3481
	$5a_1$ σ	-0.7375	-0.6738	-0.6340	-0.6180	-0.6156	-0.6142
	$5b_2$ σ	-0.6045	-0.6097	-0.6134	-0.6158	-0.6155	-0.6142
	$1b_1$ π	-0.6549	-0.6260	-0.6206	-0.6170	-0.6155	-0.6142
	$1a_2$ π	-0.6010	-0.6132	-0.6168	-0.6166	-0.6155	-0.6142
	$6a_1$ n	-0.6583	-0.6140	-0.5933	-0.5690	-0.5622	-0.5604
	$6b_2$ n	-0.3643	-0.4774	-0.5270	-0.5576	-0.5617	-0.5604
Trans	Energy	-225.2582	-225.3229	-225.3455	-225.3487	-225.3503	-225.3503
	$5a_g$ σ	-0.7201	-0.6733	-0.6322	-0.6173	-0.6168	-0.6161
	$5b_u$ σ	-0.6673	-0.6267	-0.6179	-0.6158	-0.6167	-0.6161
	$1a_u$ π	-0.6409	-0.6234	-0.6199	-0.6167	-0.6167	-0.6161
	$1b_g$ π	-0.5822	-0.6109	-0.6162	-0.6163	-0.6167	-0.6161
	$6a_g$ n	-0.6021	-0.5995	-0.5910	-0.5692	-0.5621	-0.5601
	$6b_u$ n	-0.4149	-0.4900	-0.5318	-0.5584	-0.5617	-0.5601

[a] The 30.0 bohr cis and trans energies differ because R_{C-O} is different in optimized cis and trans glyoxal.

[b] R_{opt} is the carbon-carbon optimized bond length in cis or trans glyoxal.

TABLE VI. Mulliken populations. The Mulliken populations for valence glyoxal molecular orbitals are shown broken down in atomic orbital types. The values are for one of the two equivalent centers: oxygen, carbon, or hydrogen.

		n_a	π_b	n_b	π_a
		trans-Glyoxal			
Oxygen	s	0.000	-	0.000	-
	p	0.630	0.732	0.818	0.536
Carbon	s	0.004	-	0.049	-
	p	0.192	0.267	0.043	0.464
Hydrogen	s	0.174	-	0.090	-
		cis-Glyoxal			
Oxygen	s	0.000	-	0.002	-
	p	0.639	0.526	0.820	0.713
Carbon	s	0.005	-	0.046	-
	p	0.185	0.474	0.040	0.287
Hydrogen	s	0.171	-	0.092	-

FIGURE CAPTIONS

Figure 1. Glyoxal geometries.

Figure 2. Qualitative representation of glyoxal n and π molecular orbitals. The combination of carbon and oxygen atomic p orbitals produces n and π orbitals localized on each CO. In a planar dicarbonyl, the π degeneracy is lost and the perpendicular components combine in phase or with opposite phase as indicated by the shading.

Figure 3. Internal rotation potential curve.

Figure 4. Glyoxal orbital energies. Because of the reduction to C_2 symmetry in the gauche forms, the n and π designations are inappropriate for other than the planar forms. The reduction in symmetry also makes possible the correlation of cis n orbitals with trans π orbitals, etc.

Figure 5. Interaction of two CO molecules. The breakdown of localized n and π molecular orbital symmetry is indicated by the plots of orbital energies with varying CO-CO distance. The CO molecules were held in a planar arrangement, either cis or trans, with the C-C-O angle and C-O bond length being those of the analagous optimized cis or trans glyoxal structures.

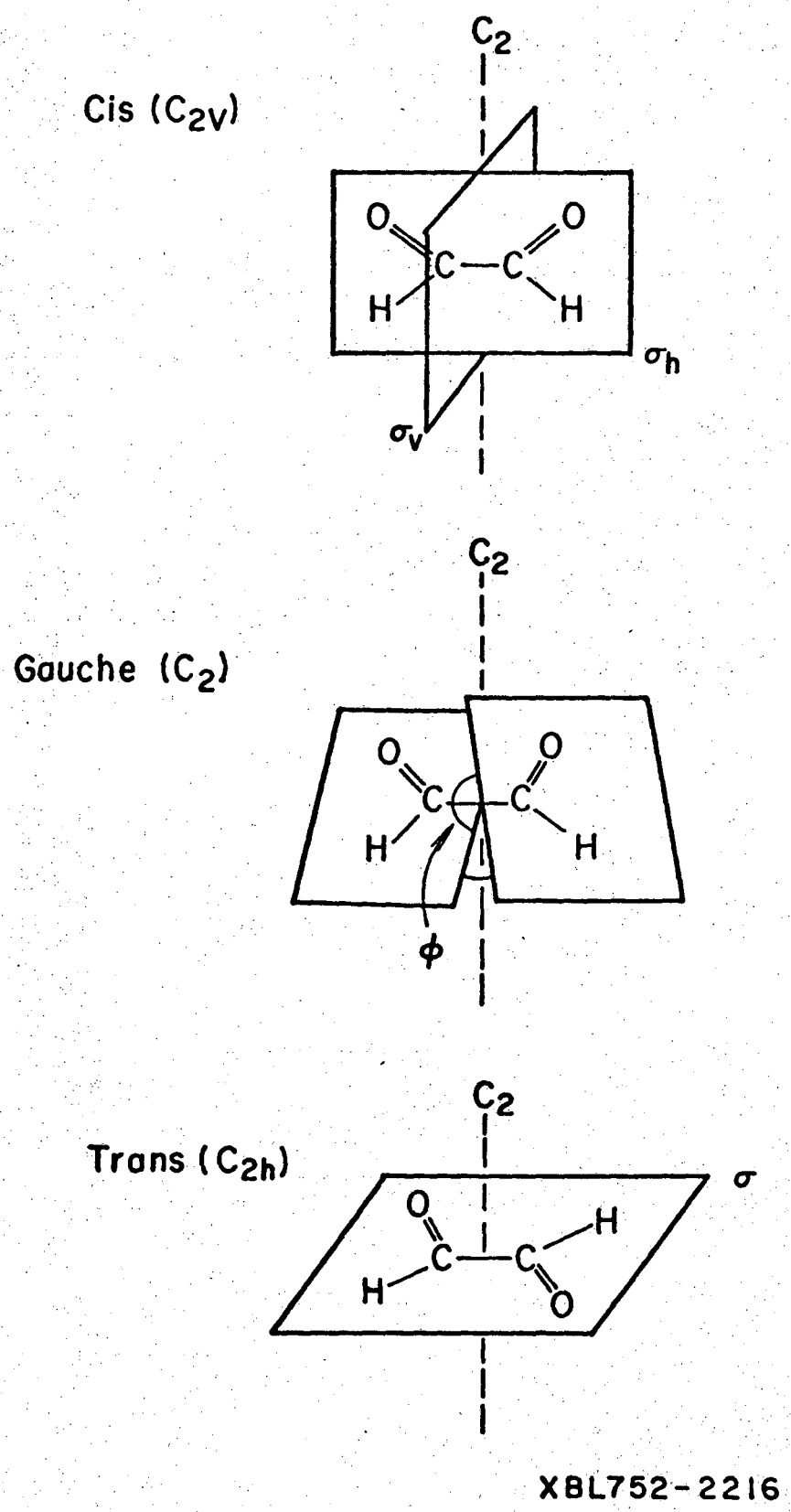
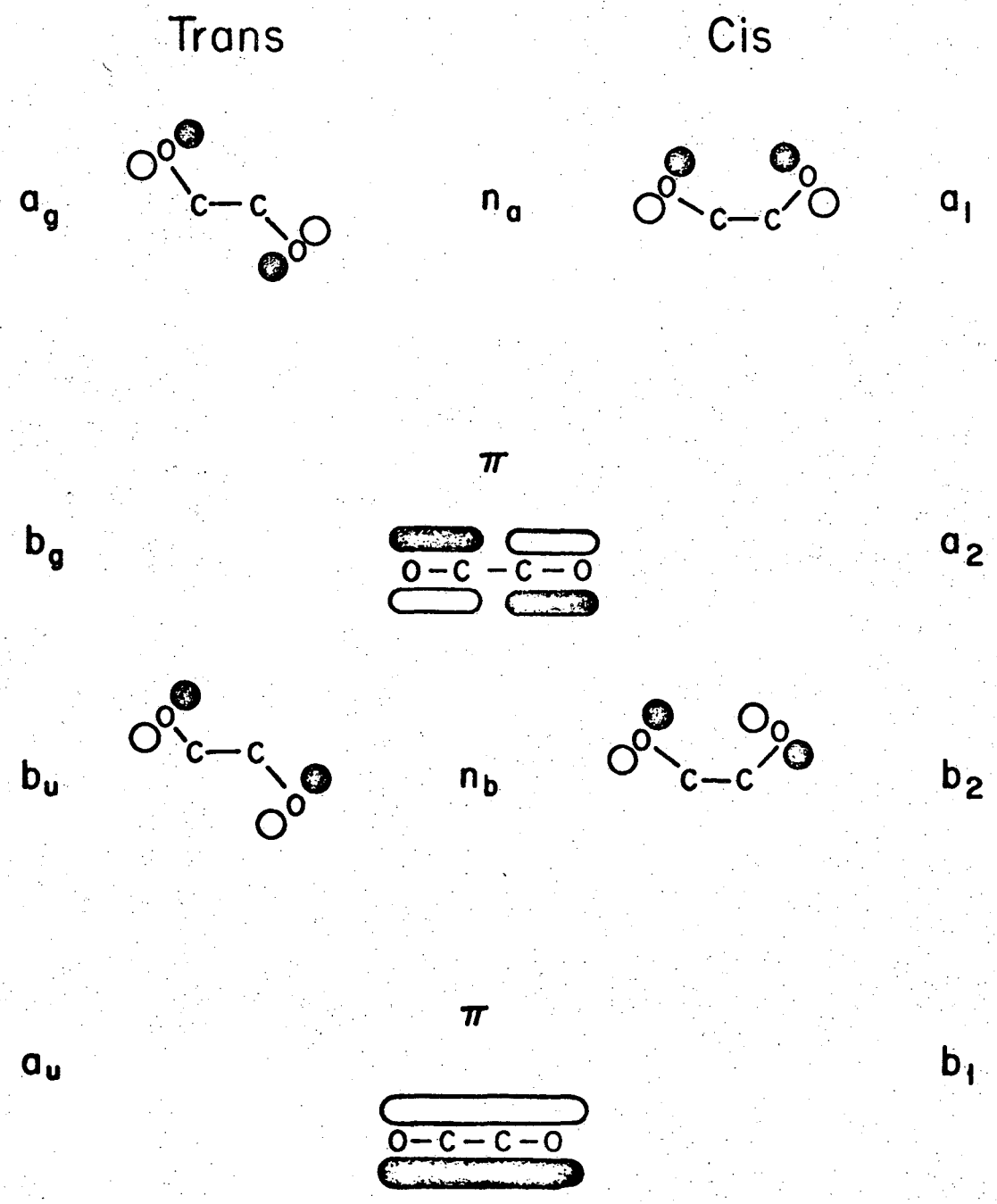

Cis (C_{2V})
C_2
O
O
C
C
H
H
σ_h
σ_v
Gauche (C_2)
C_2
O
O
C
C
H
H
ϕ
Trans (C_{2h})
C_2
σ
O
H
C
C
H
O
XBL752-2216

Fig. 1



n orbitals are in-plane

XBL752-2213

Fig. 2

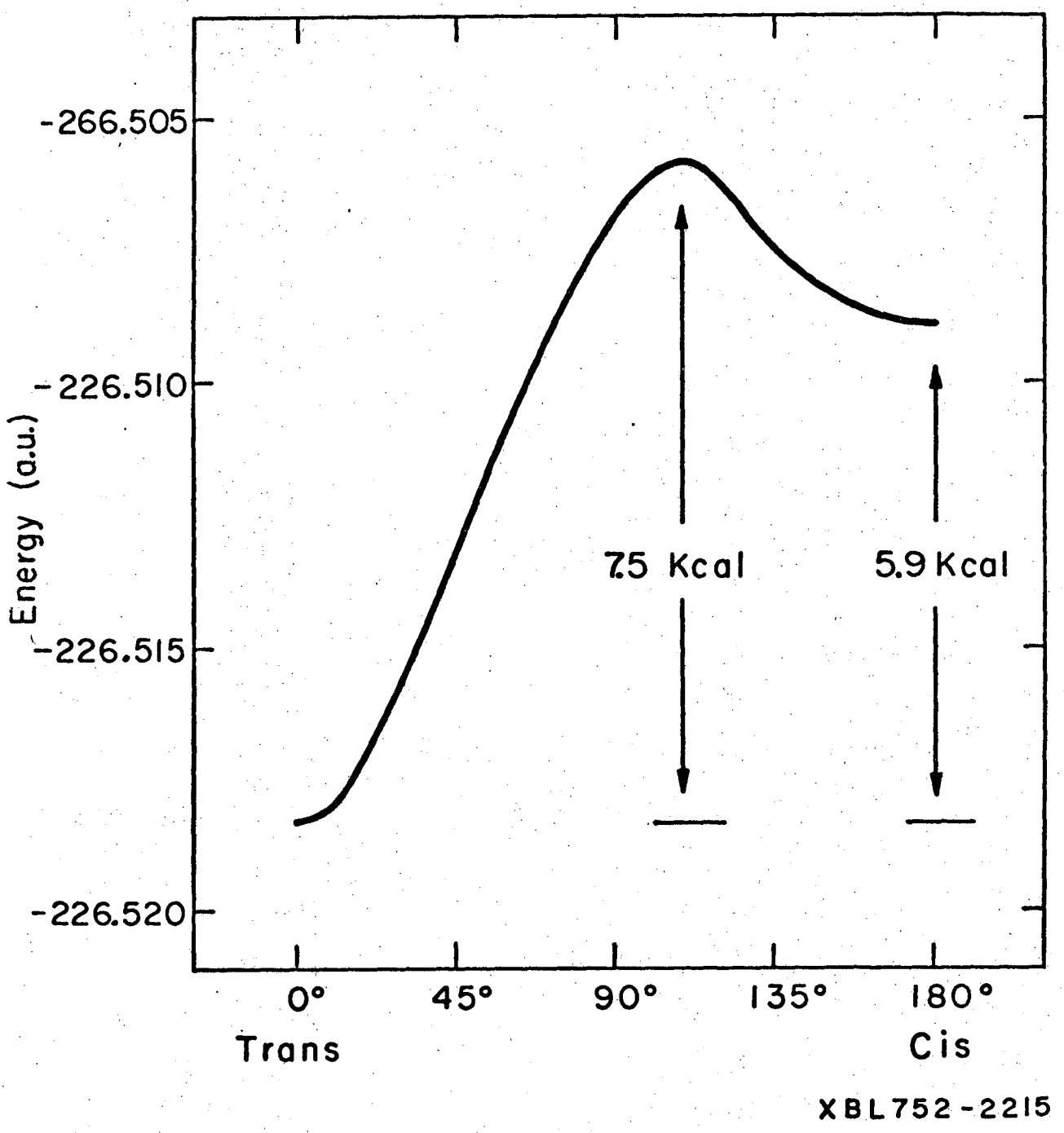

-266.505
-226.510
-226.515
-226.520
Energy (a.u.)
7.5 Kcal
5.9 Kcal
0°
45°
90°
135°
180°
Trans
Cis
XBL752-2215

Fig. 3

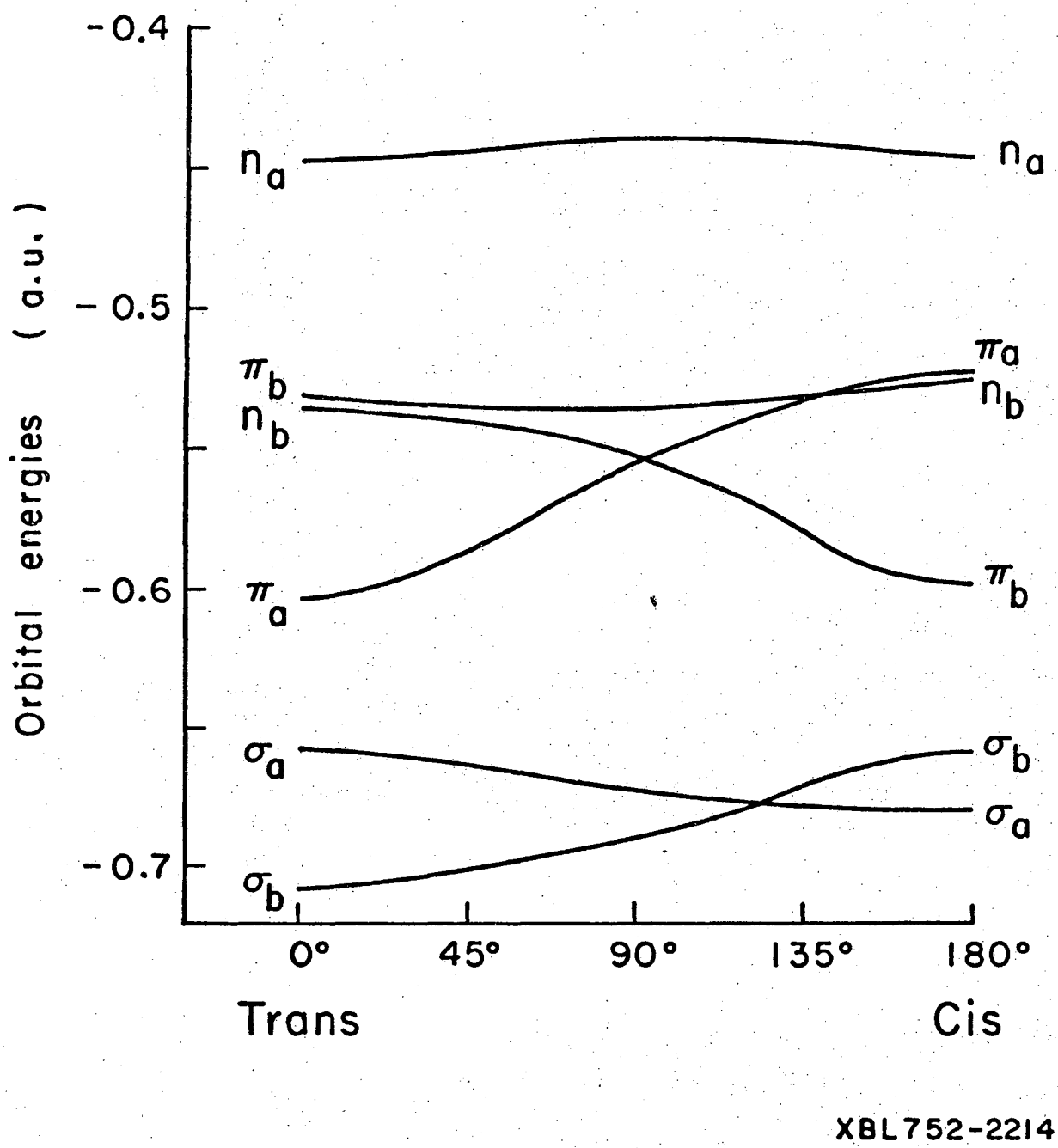
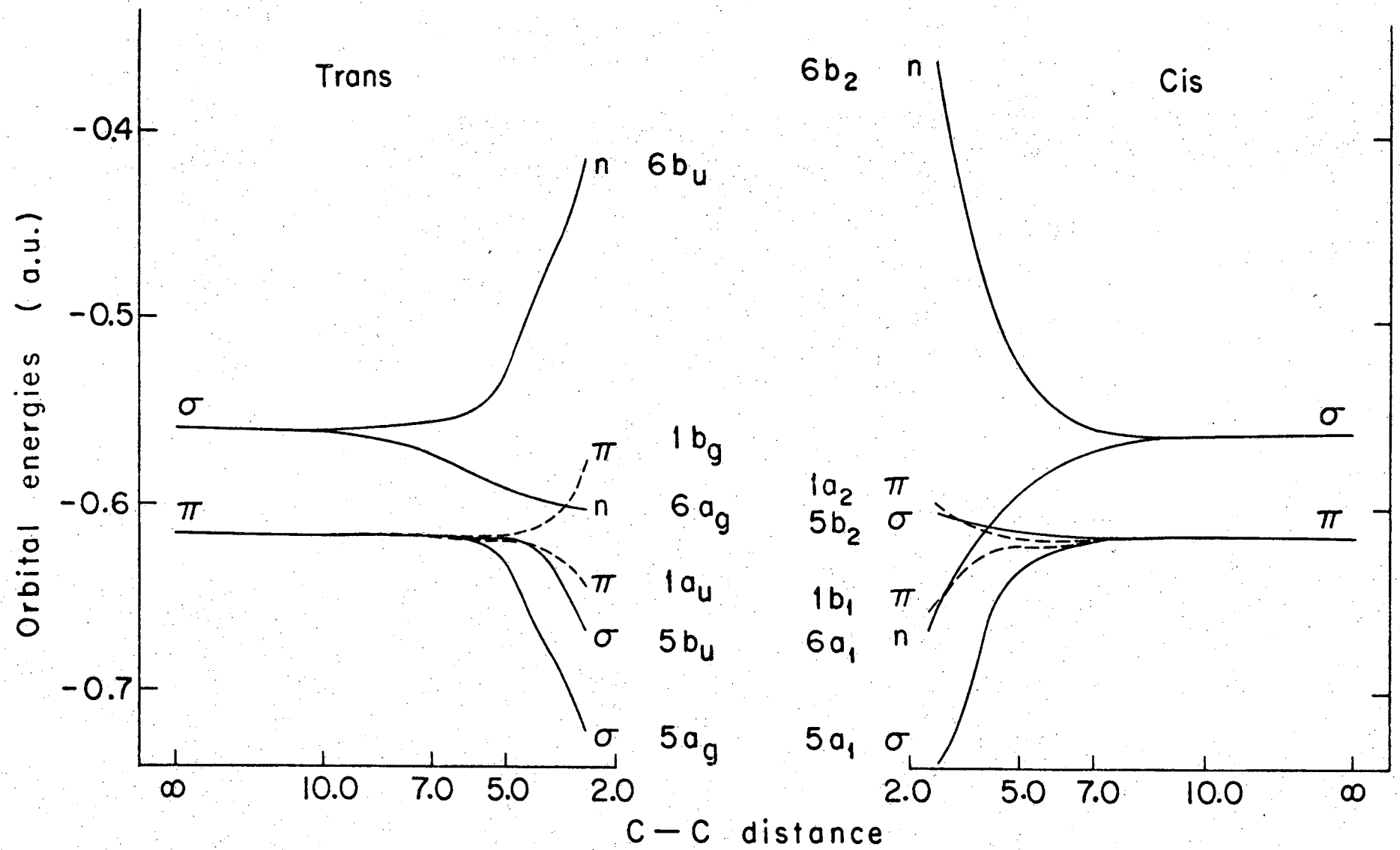

-0.4
-0.5
-0.6
-0.7
Orbital energies (a.u.)
n_a
π_b
n_b
π_a
σ_a
σ_b
n_a
π_a
n_b
π_b
σ_b
σ_a
0°
45°
90°
135°
180°
Trans
Cis
XBL752-2214

Fig. 4



XBL752-2217

Fig. 5

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720