and *gauche* forms, respectively. Their mean value, 1.72 D, agrees fairly well with the observed 1.39 D in benzene solution.[10] Therefore, the electron density calculated by the CNDO method may be reliable and can be used as the basis of our research. This conclusion, in turn, suggests the possibility of applying the LCBO–MO theory as a semiempirical one to the compounds other than alkanes.

Acknowledgment. The authors express their sincere thanks to Dr. Keiji Kuwata for his discussions.

(10) P. Trunel, *Compt. Rend.*, **203**, 563 (1936).

Ground- and Excited-State Geometries of Benzophenone

by Roald Hoffmann and Jerrald R. Swenson

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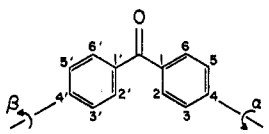
The equilibrium geometries of benzophenone and benzaldehyde in ground and (n,π^*) excited states are calculated using the extended Hückel and CNDO/2 methods. The ground state of benzophenone has both phenyl rings twisted out of plane to a C_2 geometry by 38°. The excited state has a considerably steeper potential well for a similar geometry in which the angles of twist are 32°. It appears that the carbonyl group remains locally planar in the excited state. Potential surfaces for the interconversion of enantiomeric minima are reported.

Introduction

Among photochemists benzophenone (**1**) is a most popular molecule. Careful and elegant studies have clarified the mechanism of the classic photochemical reduction of benzophenone to benzpinacol in the presence of hydrogen donors.[1] Benzophenone participates in a



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number of photochemical 2 + 2 cycloadditions yielding oxetanes,[2] but perhaps the greatest utility of benzophenone is found in its application as an agent for efficient triplet state energy transfer.[3] Equilibrium geometry changes in the excited states of molecules play a most significant role in determining their photochemical behavior. In this contribution we examine possible geometry changes in the (n,π^*) excited state of benzophenone.

The ground-state equilibrium geometry of benzophenone is determined by a balance of steric and conjugative effects. Conjugation of the carbonyl group with the phenyl rings would favor a planar conformation. Steric repulsion between the H_2 and H_2' hydrogen atoms prevents the attainment of coplanarity. Each of the phenyl rings must then be rotated by some angle, α and β (see structure **1**), out of the plane formed by the carbonyl group and the adjacent phenyl carbon atoms. The mode of rotation which most efficiently relieves the steric problems of the planar geometry is a conrotatory one, *i.e.*, α and β as defined in structure **1** both positive and probably of similar magnitude. This was clearly pointed out by Adams,[4] Rodebush,[5] and Jones[6] though the steric prohibition to coplanarity was no doubt apparent to many researchers as soon as the structure of optically active biphenyls was clarified.[7]

(1) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1530 (1901); C. Weizmann, E. Bergmann, and Y. Hirschberg, *J. Amer. Chem. Soc.*, **60**, 1530 (1938); H. L. J. Bäckström, *Z. Phys. Chem.*, **B25**, 99 (1934); H. L. J. Bäckström and K. Sandros, *Acta Chim. Scand.*, **14**, 48 (1960); A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947); G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); A. Beckett and G. Porter, *ibid.*, **59**, 2039, 2051 (1963); W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2471 (1962); J. A. Bell and H. A. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(2) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); D. Scharf and F. Korte, *Tetrahedron Lett.*, 821 (1963); G. O. Schenck, W. Hartmann, and R. Steinmetz, *Ber.*, **96**, 498 (1963); R. Steinmetz, W. Hartmann, and G. O. Schenck, *ibid.*, **98**, 3854 (1965); J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966); J. W. Hanifin and E. Cohen, *Tetrahedron Lett.*, 1419 (1966); D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964); N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1965); D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968), and references therein.

(3) Reviewed by A. Terenin in "Recent Progress in Photobiology," E. J. Bowen, Ed., Blackwells, London, 1965, p 3; V. L. Ermolaev, *Usp. Fiz. Nauk*, **80**, 3 (1963).

(4) J. F. Hyde and R. Adams, *J. Amer. Chem. Soc.*, **50**, 2499 (1928); M. E. Maclean and R. Adams, *ibid.*, **55**, 4683 (1933).

(5) M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940).

(6) R. N. Jones, *ibid.*, **67**, 2127 (1945).

Intensity effects on the electronic spectrum of benzophenone were cleverly utilized as a means of obtaining an estimate of the angle of twist of the phenyl groups.[8,9]

Crystal structures of substituted benzophenones[10-13] exhibited approximately equal angles of twist of each ring in the range of 20–35°. The most precise of these[11b] has slightly differing angles: $\alpha \simeq 25°$, $\beta \simeq 35°$. Recently crystal structures of benzophenone itself have become available.[14,15] A dihedral angle of 56° between the two phenyl rings is reported.[15] Assuming C_2 molecular symmetry, this corresponds to $\alpha = \beta = 33°$.

Discussion

We have carried out approximate molecular orbital calculations of two types—CNDO/2[16] and extended Hückel[17] (EH)—on benzophenone.[18] The first degree of freedom we studied was the conrotatory (C_2 molecular symmetry, $\alpha = \beta$) twisting of the phenyl rings away from the molecular plane. Figure 1 shows the calculated EH results for the ground state and the excited configuration resulting from (n,π^*) excitation. The ground state has a shallow minimum at $\alpha = \beta = 38°$; the excited configuration has a much deeper minimum at a significantly smaller angle of twist, $\alpha = \beta = 32°$. The agreement with the ground-state crystallographic[15] value of $\alpha = \beta = 33°$ is good, and the calculations thus produce the balance of steric and conjugative effects which produces the equilibrium geometry.[19] The CNDO/2 method gave an energy minimum at $\alpha = \beta = 90°$. Similar results were obtained for benzaldehyde. Since the discrepancy with experiment is sizable, we did not pursue calculations with this method any further.

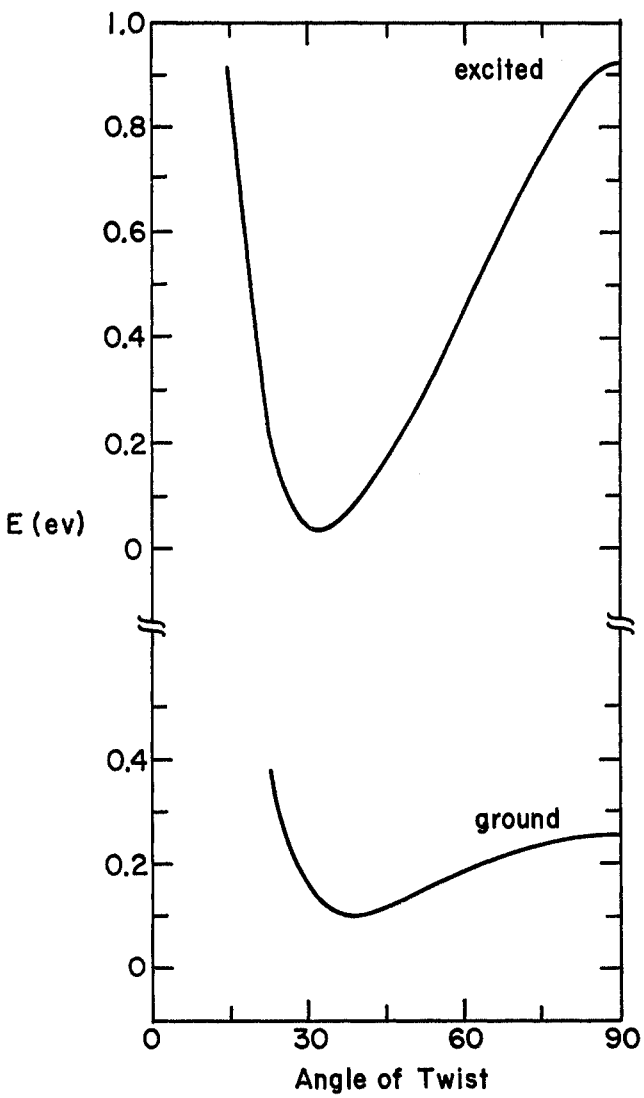


Figure 1. Extended Hückel potential energy curves for the conrotatory twisting of phenyl rings in ground and excited configurations of benzophenone. The energy scale is relative to an arbitrary energy zero, and one different for ground and excited configurations. (Note broken energy scale.)

Since unsymmetrical geometries ($\alpha \neq \beta$) have been suggested at various times,[20] we thought it important to allow the molecule the freedom of varying α and β independently. Figure 2 illustrates our calculated potential energy surface for the ground state. The figure shows the range $-90° < \alpha < +90°$, $0° < \beta < 180°$. Other conformations are identical by symmetry with those shown in Figure 2; in fact the only symmetry nonequivalent regions or generators of the figure are two tri-

(7) A fascinating contemporary discussion of this important chapter in the development of modern structural ideas may be found in E. E. Turner and R. J. W. Le Fèvre, *Chem. Ind.* (London), **45**, 831, 883 (1926); F. Bell and J. Kenyon, *ibid.*, **45**, 864 (1926); W. H. Mills, *ibid.*, **45**, 884 (1926); J. Kenner, *ibid.*, **46**, 218 (1927); see also R. Adams and H. C. Yuan, *Chem. Rev.*, **12**, 260 (1933).

(8) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); E. A. Braude and F. Sondheimer, *ibid.*, 3754 (1954).

(9) R. F. Rekker and W. Th. Nauta, *Rec. Trav. Chim.*, **73**, 969 (1954); **80**, 764 (1961); *Spectrochim. Acta*, **8**, 348 (1957).

(10) 4,4′-Dichlorobenzophenone: J. Toussaint, *Proc. Soc. Roy. Sci. Liege*, **17**, 10 (1948).

(11) 4,4′-Dimethoxybenzophenone: (a) I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *Acta Cryst.*, **10**, 481 (1957); (b) H. G. Norment and I. L. Karle, *ibid.*, **15**, 873 (1962).

(12) 3,3′-Dibromobenzophenone: S. Ramaseshan and K. Venkatesan, *Experientia*, **14**, 237 (1958).

(13) 2,2′-Dibromo-4,4′,5,5′-tetramethoxybenzophenone: A. Olivi and A. Ripamonti, *Ric. Sci.*, **28**, 2102 (1958).

(14) E. B. Vul and G. M. Lobanova, *Kristallografiya*, **12**, 411 (1967); *Soviet Phys.-Cryst.* (English Transl.), **12**, 355 (1967).

(15) E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).

(16) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(17) R. Hoffmann, *ibid.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964); *Tetrahedron*, **22**, 521, 539 (1966), and subsequent papers. In our present calculations we use a hydrogen 1s exponent of 1.3.

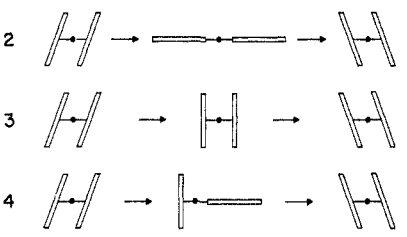
(18) We assumed an idealized benzophenone geometry in all our calculations: C=O, 1.25 Å; C(carbonyl)–C(phenyl), 1.50 Å; hexagonal benzene rings with C–C, 1.40 Å; C–H, 1.10 Å; angle C_1CC_1' 120°.

(19) Faithful modeling of the very similar balance in phenyl carbonium ions has also been obtained: R. Hoffmann, R. Bissell, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969).

(20) *E.g.*, W. D. Chandler and L. Goodman, *J. Chem. Phys.*, **45**, 4088 (1966); for a review of these suggestions see J. Barassin, G. Queguiner, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 4707 (1967).

angles: a conrotatory region, $0° < \alpha < 90°$, $0° < \beta < \alpha$ and a disrotatory region $-90° < \alpha < 0°$, $0° < \beta < |\alpha|$. The only minima in this surface are the previously located conrotatory one at $\alpha = \beta = 38°$, and its mirror image, at $\alpha = -38°$, $\beta = 142°$. There are no minima in the disrotatory regions, and geometries such as those with $\alpha = 0°$, $\beta = 90°$ or $\alpha = \beta = 90°$ are saddle points.

The stable conformation of benzophenone is chiral. There arises immediately the problem of mechanisms for the conversion of one enantiomer into the other and the activation energies for such processes. As in the analogous diphenyl methyl system,[19] we consider three possible geared motions for the conversion of one enantiomer into the other. These are shown schematically below. In mechanism 2 the transition state is planar



($\alpha = \beta = 0°$); in 3 both phenyl rings are perpendicular to the plane of the carbonyl carbon atom ($\alpha = 90°$, $\beta = 90°$); in 4 one phenyl ring is coplanar and the other is perpendicular ($\alpha = 0°$, $\beta = 90°$). Figure 2, previously presented, contains the requisite information to compare the three reaction paths. Mechanism 2, involving the sterically hindered planar intermediate, has an extremely high activation energy of 3.682 eV. Mechanism 4 is slightly favored over mechanism 3; the calculated activation energy is 0.146 eV for 3 and 0.051 eV for 4. The calculated activation energy for 4 is very small, and the conversion from one enantiomeric form of benzophenone into the other should proceed most easily.

The experimental information available to date on benzophenone clearly demands a small barrier. It is clear that bulky substituents on the benzene rings will increase the barriers to interconversion.[21]

We now turn to a discussion of the excited state. Figure 3 illustrates the extended Hückel surface for the (n,π^*) excited configuration of benzophenone. The angles are defined analogously to Figure 2, but the energy contours are spaced at greater energy intervals. The only minima in this surface are once again the conrotatory ones for $\alpha = \beta = 32°$ and $\alpha = -32°$, $\beta = 148°$. Loci such as $\alpha = 0°$, $\beta = 90°$ remain saddle points. New saddle points occur in the disrotatory regions, *e.g.*, at $\alpha = -57°$, $\beta = 57°$ and $\alpha = 57°$, $\beta = 123°$.

The preference of the excited (n, π^*) configuration for a more nearly planar geometry is significant. The results were anticipated from the examination of the interaction diagram in Figure 4. On the left side of the

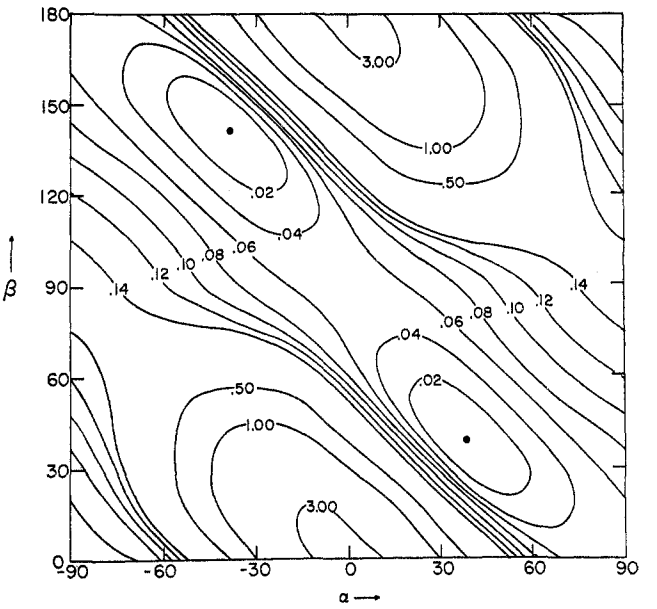


Figure 2. Contour diagram of the extended Hückel potential energy surface for the ground state of benzophenone. The signs of α and β are defined relative to the sense of rotation shown in structure 1. α and β are equal to zero for the planar conformation. The energy contours are in electron volts relative to the marked minima.

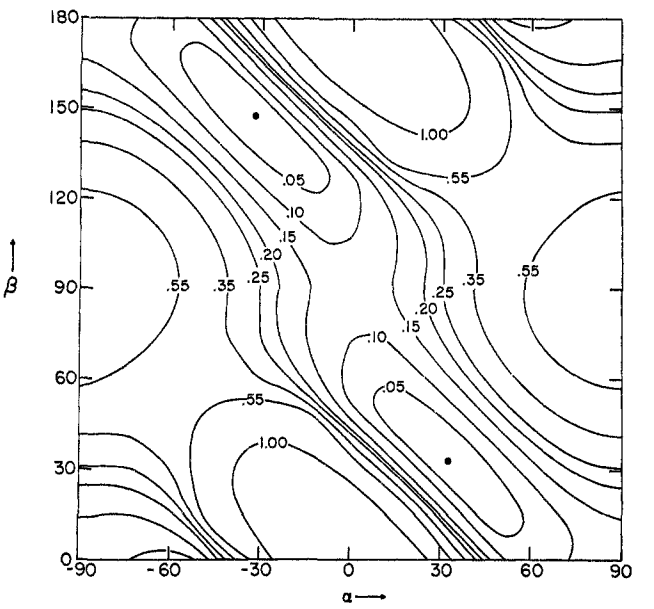
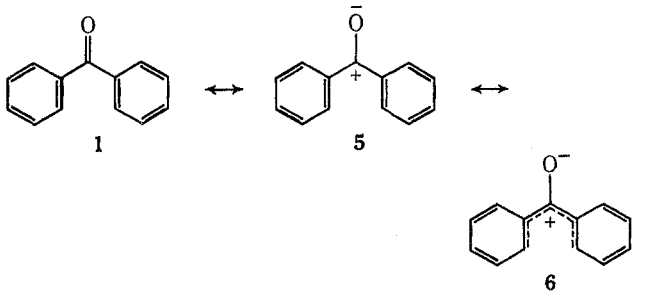


Figure 3. Contour diagram of the extended Hückel potential energy surface for the (n,π^*) excited configuration of benzophenone. See caption to Figure 2 for definition of angles. (Note that the contours in Figure 3 are at greater energy intervals than in Figure 2.)

(21) D. Lauer and H. A. Staab, *Ber.*, **102**, 1631 (1969); *Tetrahedron Lett.*, 177 (1968), report some careful studies of such highly hindered benzophenones. Adams (ref 4) attempted to resolve some less hindered derivatives without success. The resolution of a substituted benzophenone has recently been reported: K. V. Narayanan, R. Selvarajan, and S. Swaminathan, *J. Chem. Soc., C*, 540 (1968). This result has been questioned by Lauer and Staab (ref 21).

diagram are the benzene π orbitals, taken twice. On the right side are carbonyl π and π^* orbitals. As a consequence of the greater electronegativity of the oxygen atom the center of energy of the carbonyl orbitals is lower than that of the benzene orbitals. The molecular orbitals may be classified as symmetric, S, or antisymmetric, A, with respect to the molecular C_2 axis. The molecular orbitals are then allowed to interact; minimum interaction would correspond to $\alpha = \beta = 90°$, maximum π-electron interaction would occur at $\alpha = \beta = 0°$. The principal interaction is that of the carbonyl π^* with an unoccupied benzene orbital of the same symmetry. In the resulting stabilized MO, which is principally carbonyl π^*, the benzene π^* MO is mixed in a bonding way. Population of this MO in the (n,π^*) excited state results in both an increase in $C-C_1$ and $C-C_1'$ bond order and a greater tendency to planarity. The relative depths of ground- and excited-state minima are explained in the same manner. The interaction of benzene and carbonyl orbitals has been previously analyzed with the aid of an interaction diagram.[22,23]

The preceding argument may also be used to account for the stabilization of the disrotatory region as manifested by the removal of the ground-state saddle point at $\alpha = -90°, \beta = 90°$ to $\alpha = -57°, \beta = 57°$. However, in the excited state, the disrotatory region may benefit from another electronic interaction, arising from the proximity of the two benzene rings. The polar valence bond structures **5** and **6** no doubt contribute to the best description of benzophenone. Pentadienyl cations, such as may be seen in part of structure **6**, are expected theoretically[24] and known experimentally[25] to undergo electrocyclic ring closure to cyclopentenyl cations in a conrotatory manner in the ground state and in a disrotatory manner in the excited state. The stabilizing interaction here is from the overlap of the C_2 and C_2' 2p orbitals.



The singlet and triplet (n,π^*) states of formaldehyde[26] are pyramidal. We therefore studied the feasibility of the similar distortion in benzophenone excited states. CNDO/2 results for the formaldehyde excited-state geometry have been presented by Kroto and Santry.[27] The calculated barrier to inversion is small. EH calculations predict an out-of-plane angle of 20° and an inversion barrier of 0.0034 eV. The singlet state has in fact been analyzed to have the oxygen out of the plane of the remaining atoms by 20° and to possess an inversion barrier of ~650 cm^{-1} or 0.080 eV.[26b] Thus both computational methods give much too small inversion barriers, though they confirm nonplanarity.

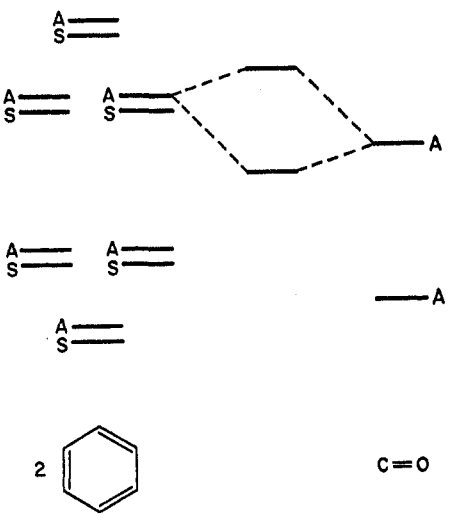


Figure 4. The interaction of the π levels of two phenyl groups with a carbonyl group, as in benzophenone. The levels are classified according to their behavior under C_2. Only the most significant interaction is shown.

For the equilibrium conformation of the excited configuration of benzophenone ($\alpha = \beta = 32°$) we studied a motion of the carbonyl oxygen out of its local molecular plane. The resulting potential energy curve (EH) is compared with that of formaldehyde in Figure 5. The planar conformation remains stable. However, in view of the fact that the EH method severely underestimates the barrier to inversion in formaldehyde, the only reliable conclusion that may be drawn is that the out-of-plane angle in benzophenone (if nonzero at all) is less than it is in formaldehyde.

We also studied an out-of-plane motion of the oxygen at the disrotatory saddle point at $\alpha = -57°, \beta = 57°$. It was found that in the excited state the carbonyl oxygen definitely preferred to move out-of-plane, coming to an equilibrium position bent by 25° down,

(22) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955); J. Tanaka, S. Nagakura, and M. Kobayashi, *ibid.*, **24**, 311 (1956).

(23) H. Suzuki, "Electronic Absorption Spectra and Geometries of Organic Molecules," Academic Press, New York, N. Y., 1967, p 440; H. Suzuki, *Bull. Chem. Soc. Jap.*, **35**, 1853 (1962); **33**, 613 (1960).

(24) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); *Angew. Chem.*, in press; R. Hoffmann and R. B. Woodward *Accounts. Chem. Res.*, **1**, 17 (1968).

(25) R. B. Woodward, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 217. D. Kurland, Dissertation, Harvard, 1967; R. Lehr, Dissertation, Harvard, 1968.

(26) (a) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958); *J. Chem. Phys.*, **31**, 1678 (1959); (b) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956); (c) V. A. Job, V. Sethuraman, and K. K. Innes, *J. Mol. Spectrosc.*, **30**, 365 (1969).

(27) H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 792, 2736 (1967).

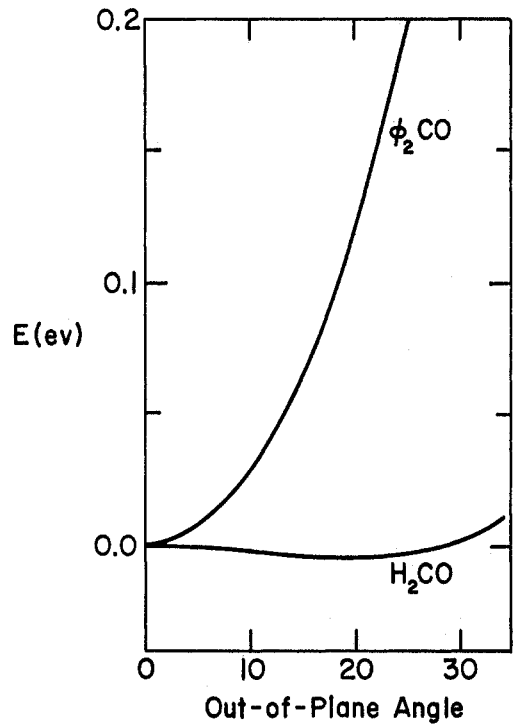


Figure 5. Comparison of calculated out-of-plane bending energy curves of formaldehyde and benzophenone. Both molecules are referred to the same energy zero for a planar geometry. The bending angle is defined in the plane perpendicular to the XCX plane and containing the bisector the XCX of angle. The bending angle is then the angle in the above defined plane by which the oxygen is out of planarity.

i.e., below the original plane defined by structure **1**. This placed the oxygen closest to the 6 and 6′ positions. The favored geometry was 0.25 eV below the "planar" excited-state conformation. This is still 0.22 eV above the conrotatory excited-state minima at $\alpha = \beta = 32°$. Readjustment of α and β in the "nonplanar" disrotatory conformation gain only approximately 0.01 eV, so that we remain confident that the only true minima in the excited state are the "planar" conrotatory ones.

The preferred direction of out-of-plane bending at the disrotatory saddle point is nevertheless interesting. One possible explanation of the observed trend may be

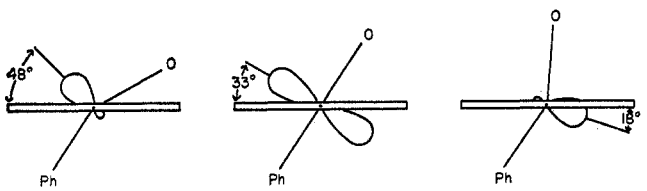


Figure 6. Projection of the left-hand phenyl ring and carbonyl oxygen on the plane perpendicular to the C_1–C_4 axis. The view is from C_4 toward C_1. The front bar is the projection of the right-hand phenyl ring. Three oxygen positions are shown. In the middle we have the disrotatory saddle point geometry, $\alpha = -57°$, $\beta = 57°$, oxygen "planar." At the left the oxygen has been moved "down" 25° (see text and caption to Figure 5), at right "up" 25°.

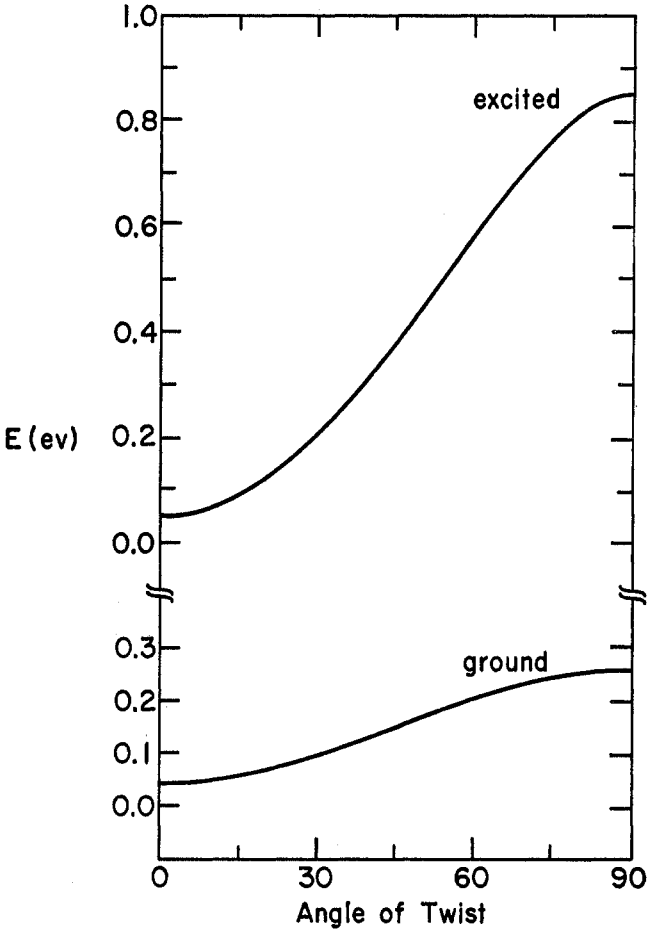
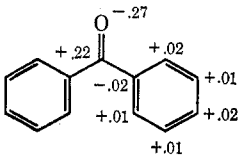


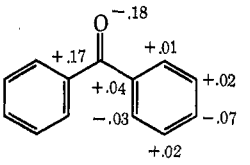
Figure 7. Energy as a function of angle of twist for ground and excited configuration of benzaldehyde. The energy scale is relative to an arbitrary energy zero, different for the two configurations. (Note broken energy scale.)

obtained from examining Figure 6. This shows a projection of C_1, and the carbonyl group on the plane perpendicular to C_1–C_4, for the "planar" disrotatory saddle point, and the two possible motions of an oxygen 25° out of plane. It is clear that better conjugation or overlap of the carbonyl carbon orbital (presumably a hybrid with increasing s character) and the phenyl orbitals is achieved upon oxygen bending in the manner indicated at left.

Our calculations also yielded the ground and excited configuration charge distributions for benzophenone. We consider the CNDO charge distributions more reliable and show below the carbon and oxygen charges computed by this method for a conrotatory geometry with $\alpha = \beta = 35°$



ground-state charge distribution



excited-state charge distribution

The charge redistribution in the excited state is not very great. This is the consequence of an "n" orbital which is not localized at oxygen, but significantly delocalized thoughout the molecule. The absence of charge redistribution of a magnitude consistent with the classical picture of a fully localized oxygen lone pair is supported by recent measurements of the dipole moments of benzophenone excited states.[28]

Benzaldehyde has been assumed to have a planar conformation since there is no steric interaction preventing such a conformation. Extended Hückel calculations confirm this assumption. The potential energy curves for the rotation of the aldehyde group away from the plane of the phenyl ring for the ground state and the excited state of benzaldehyde arising from the carbonyl (n,π^*) transition are shown in Figure 7. The calculated barrier to rotation is 0.22 eV for the ground state and 0.79 eV for the excited state. The theoretical analysis is just like that presented for benzophenone, with a predicted higher barrier to internal rotation in the (n,π^*) excited state compared to the ground state.

Acknowledgment. This work was supported by the Petroleum Research Fund of the American Chemical Society and the Public Health Service (GM 13468).

(28) R. M. Hochstrasser and T. S. Lin, *J. Chem. Phys.*, **49**, 4929 (1968).

Energy Parameters in Polypeptides. II. Semiempirical Molecular Orbital Calculations for Model Peptides[1,2]

by J. F. Yan, F. A. Momany,[3] R. Hoffmann, and H. A. Scheraga[4]

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The EHT and CNDO/2 methods have been used to compute charge distributions, dipole moments, energies for internal rotation, electronic orbital configurations, and electronic spectra of formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, and acetyl-L-proline amide. The CNDO/2 method gives more reliable charge distributions and dipole moments than the EHT procedure. However, the EHT procedure is better for treating internal rotation and provides a physical picture for the preference of the *trans* form of the amide group in peptides. Calculations are also carried out for the changes in the charge distributions, dipole moments, energies for internal rotation, electronic orbital configurations, and electronic spectra of these model compounds as the amide group departs from planarity. Some of the data for acetyl-L-prolineamide are represented in the form of a ψ–ω energy contour diagram.

Introduction

At the present time, conformational energy calculations are being carried out for polypeptides, using *empirical* methods.[5] In conjunction with these studies, an examination is being conducted[6,7] of the underlying theoretical basis of the empirical approaches.

In the first paper[8] of this series (designated here as paper I), a semiempirical method was employed to obtain some of the parameters required for the conformational energy calculations. The method of Del Re[9–11] was used to obtain the σ charges, and dipole moment data (as well as computed values of Pullman and Pullman[12]) were used to obtain the π charges. The resulting total charges on all the atoms of the amino acid residues which commonly occur in proteins were then obtained. A similar calculation of the

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(5) See, *e.g.*, H. A. Scheraga, *Advan. Phys. Org. Chem.*, **6**, 103 (1968).

(6) K. D. Gibson and H. A. Scheraga, *Physiol. Chem. Phys.*, **1**, 109 (1969).