Conformational Behaviour of Organic Carbonyl Compounds. Part 1. A Molecular Orbital Approach to the Study of Internal Rotation in Conjugated Aldehydes and Ketones

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Semi-empirical and *ab initio* MO methods are employed in a study of internal rotation of conjugated aldehydes and ketones. In general CNDO/2 does not provide a correct pattern for the energy as a function of the angle of internal rotation. The results from the semi-empirical PCILO method are more consistent with experiment. The calculated energy barriers are noticeably lower than the experimental ones. but roughly proportional. The energy barriers calculated by the *ab initio* MO approach with the minimal STO-3G basis set behave correctly as regards the relative stability of planar and perpendicular conformations, but quantitatively are not comparable with experimental values. The π-bond order for the C–C bond joining the carbonyl group to the unsaturated system for the planar conformation shows a linear correlation with the experimental free energy of activation for a large number of molecules and this is true of the values obtained both by CNDO/2 and by *ab initio* STO-3G.

BARRIERS restricting rotation around formal carbon–carbon single bonds between sp^2 hybridized carbon atoms are expected on theoretical grounds and have been detected experimentally for many classes of organic compounds. In the absence of steric interactions with other bulky substituents the coplanarity of the carbonyl and the unsaturated group to which it is bonded should represent the ground state of the molecule, while the transition state should occur when the planes of these groups are mutually orthogonal.

When a formyl or acetyl group is bonded to a molecular residue having a binary axis coincident with the direction of the bond between these groups (as for example in benzaldehyde or acetophenone) the ground state consists of two identical isomers (topomers), which in most known cases rapidly interconvert at room temperature. If symmetry is lacking in the molecular residue two isomers are in principle present which often are frozen at low temperature, and problems arise in the conformational assignment. This is the case with furan-2-carbaldehyde, which has been extensively studied,[1-7] and of several other derivatives of heterocyclic compounds.[8-11] Often the results, obtained also from various experimental techniques, are difficult to compare directly [4,9] since they are obtained in different solvents or in the gas phase and the values for the same molecule from different sources may differ.

Calculations were also employed to predict or to confirm the relative isomer stability or to analyse the chemical nature of the barrier to rotation, and in several studies experimental results have been compared with energy differences computed by empirical, semi-empirical, and *ab initio* quantum mechanical methods. The simple Hückel and the more sophisticated extended Hückel MO theory provided a good basis of comparison of the energy barriers in furan-2-carbaldehyde,[2] 2-acetylfuran,[12] and *N*-methylpyrrole-2-carbaldehyde: [13] the loss in π-electron energy upon rotation given by the Hückel method is, on the other hand, not suitable for a comparison of the free energy of activation for a large class of molecules [2] and the extended Hückel method overemphasizes the steric factors.[14] The CNDO/2,[4] INDO,[4] and NDDO [15] techniques provide reasonable energy barriers for furan-2-carbaldehyde; [4] the relative stability of conformers is correctly predicted both for furan- [4,15,16] and thiophen-2-carbaldehyde.[11] These semi-empirical methods fail [17-19] in any case to indicate as more stable the planar conformation in derivatives of benzene and of six-membered heteroaromatic compounds. Complete agreement with experiment is obtained [20a] when the PCILO computational scheme is employed. The superiority of the PCILO over the CNDO/2 method for predicting correct geometries has also been found for other molecular systems, although the reasons are not completely understood.[20b] The *ab initio* MO theory with the minimal STO-3G basis set indicates [21] for benzaldehyde and acetophenone that the planar conformation is the ground state and the perpendicular one corresponds to an energy maximum with energy differences between these states close to the experimental results and in the correct order. One of the reasons for the failure of semi-empirical methods in conformational analysis could be, in a number of cases, the lack of a good molecular geometry: especially for the transition state deviations from standard bond lengths and angles this could be critical.[22] Results from *ab initio* calculations seem more promising as seen from the limited number of calculations carried out on complex molecules at the different level of approximation which can be introduced in non-empirical treatments. Apart from the simple cases of acetaldehyde and acetone the molecules to be examined are composed of a relatively large number of ' heavy ' atoms, and calculations by non-empirical methods have to be restricted to small basis sets such as the STO-3G,[21] and geometry optimization is feasible only when restricted to a small set of parameters.

In the present study we compare the results of semi-empirical methods applied to the analysis of internal rotation for a large number of conjugated aldehydes and acetyl derivatives both with standard geometrical structures and optimized structural parameters in order to adduce a general trend in the application of these methods to the study of internal rotation and to test

TABLE 1

Experimental free energy of activation (ΔG^*), calculated energy of activation (ΔE^*), experimental free energy differences (ΔG^0),[a] and calculated energy differences (ΔE^0) [a] between conformational isomers in aldehydes (all values in kJ mol^{-1})

		Experimental		PCILO		CNDO/2		*ab initio* STO-3G	
No.	Molecule	ΔG^*	ΔG^0	ΔE^*	ΔE^0	ΔE^*	ΔE^0	ΔE^*	ΔE^0
(1)	Benzaldehyde	31.8 [b] 32.22 [c] 33.06 [d]	0	10.25 min 0°	0	5.09 min 90°	0	24.76 min 0°	0
(2)	*p*-Tolualdehyde	34.3 [b]	0	10.27 min 0°	0	3.01 min 90°	0		
(3)	Acrylaldehyde	20.30 [e] *syn*→*anti*	8.62 (ΔH^0) [e] (*anti* > *syn*)	9.00 *syn*→*anti*	5.56 (*anti* > *syn*)	4.71 [f] min 45° max 135°	3.51 (*syn* > *anti*)	26.63 *syn*→*anti*	1.03 (*anti* > *syn*)
(4)	Furan-2-carbaldehyde	45.57 [g] *anti*→*syn*	2.55 [g] (*syn* > *anti*)	12.49 *anti*→*syn*	10.43 (*syn* > *anti*)	24.32	3.09 (*anti* > *syn*)	31.51 *anti*→*syn*	3.64 (*anti* > *syn*)
(5)	*N*-Methylpyrrole-2-carbaldehyde	51.27 [h] *anti*→*syn*	5.31 [h] (*anti* > *syn*)	3.64 *anti*→*syn*	17.49 (*syn* > *anti*)	15.28 *anti*→*syn*	4.79 (*syn* > *anti*)	23.92 *anti*→*syn*	2.41 (*syn* > *anti*)
(6)	Pyridine-4-carbaldehyde	24.7 [i] 26.4 [j]	0	9.65 min 0°	0	9.88 min 90°	0	25.83 min 0°	0
(7)	Methacrylaldehyde	25.53 [e] *syn*→*anti*	8.07 (ΔH^0) [e] (*anti* > *syn*) [e,l]	7.14 *syn*→*anti*	5.40 (*anti* > *syn*)	9.20 [f] min 20° max 110°	4.95 (*syn* > *anti*)	28.49 *syn*→*anti*	0.49 (*syn* > *anti*)
(8)	*N*-Methylpyrrole-3-carbaldehyde	42.90 [m] *anti*→*syn*	3.77 [m] (*anti* > *syn*)	16.68 *anti*→*syn*	10.42 (*anti* > *syn*)	5.17 *anti*→*syn*	1.94 (*syn* > *anti*)		
(9)	*m*-Tolualdehyde	33.0 [b]	0.20 [b] (*syn* ⩾ *anti*)	10.12 *syn*→*anti*	0.08 (*syn* ⩾ *anti*)	6.54 min 90°	0.18 (*syn* ⩾ *anti*)		
(10)	Pyridine-3-carbaldehyde	30.1 [i] 29.92 [j]	1.55 [i] (*anti* > *syn*)	12.44 *anti*→*syn*	1.10 (*anti* > *syn*)	3.39 min 90°	0.49 (*anti* > *syn*)		
(11)	Pyridine-2-carbaldehyde	31.4 [i] 32.22 [j]	3.6 [i] 2.7 [j] (*anti* > *syn*)	14.50 *anti*→*syn*	4.42 (*syn* > *anti*)	2.47 [f] min 120° max 0°	2.01 (*anti* > *syn*)		
(12)	*m*-Fluorobenzaldehyde	30.7 [b]	1.07 [b] (*syn* > *anti*)	9.74 *syn*→*anti*	0.64 (*anti* > *syn*)	6.67 min 90°	0.49 (*anti* > *syn*)	26.61 *syn*→*anti*	0.14 (*anti* ⩾ *syn*)
(13)	*N*-Formylpyrrole	58.6 [n]	0	44.99 min 0°	0	24.70 min 0°	0		
(14)	*N*-Formylindole	63.1 [o]	1.48 [o] (*Z* > *E*)	41.85 *Z*→*E*	0.61 (*E* > *Z*)	29.26 *Z*→*E*	0.21 (*Z* > *E*)		
(15)	*N*-Formylcarbazole	62.0 [o]	0	41.12 min 0°	0	30.86 min 0°	0		

[a] The values in parentheses refer to the relative isomer stability. [b] T. Drakenberg, R. Jost, and J. Sommer, *J.C.S. Chem. Comm.*, 1974, 1011. [c] L. Lunazzi, D. Macciantelli, and C. A. Boicelli, *Tetrahedron Letters*, 1975, 1205. [d] F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1964, **86**, 119. [e] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.*, 1957, **A242**, 36. [f] Differences between the maximum and the minimum energy value in the rotational curve (see Figure 2), where 0° corresponds to the *syn*-conformation. [g] K. I. Dahlquist and S. Forsen, *J. Phys. Chem.*, 1965, **69**, 4062. The relative stability *syn* > *anti* refers to polar liquids, while it should be reversed in non-polar liquids and in the gas phase.[3] [h] L. Arlinger, K. I. Dahlquist, and S. Forsen, *Acta Chem. Scand.*, 1970, **24**, 672. [i] T. Drakenberg, *J.C.S. Perkin II*, 1976, 147. [j] L. Lunazzi, D. Macciantelli, and G. Cerioni, *J.C.S. Perkin II*, 1976, 1791. [l] G. Montaudo, S. Caccamese, V. Librando, and P. Maravigna, *Tetrahedron*, 1973, **29**, 3915. [m] M. C. Fourniè-Zaluski, C. Joureguiberry, and B. Roques, *Tetrahedron Letters*, 1973, 4177: values referred to the *N*-t-butyl derivative. [n] T. Matsuo and H. Shosenji, *Chem. Comm.*, 1969, 501. [o] J. Elguero, C. Marzin, and M. E. Peek, *Org. Magnetic Resonance*, 1975, **6**, 445; the free energy difference ΔG^0 was obtained from the $E : Z$ isomer ratio.

their limits. The CNDO/2,[23] PCILO [24] and, in some cases INDO,[23] are extensively employed. We have discarded the extended Hückel approximation,[14] since criticisms of the application of this method to rotational problems have already been reported.[25,26]

The semi-empirical results are compared with those obtained from an *ab initio* STO-3G calculation and the effect of geometry optimization and basis set implementation for the smaller molecules is also taken into account in order to gain confidence in employing these methods on a general scale for discussing the problem of internal rotation in conjugated carbonyl compounds.

RESULTS AND DISCUSSION

The molecules examined, experimentally determined energy barriers (free energy of activation), and relative conformer stabilities are collected in Tables 1 and 2 for aldehydes and acetyl derivatives, respectively. All the experimental results were gathered from literature sources: energy values are expressed in kJ mol^{-1}.

The experimental determinations from various sources, apart from the fact that they sometimes refer to non-homogeneous experimental conditions, often differ in the values obtained; thus several values are often reported in Tables 1 and 2 for the same compound. This could be an indication of the range which includes the best value for a given molecule: in a few cases the interval ranges over 3—4 kJ mol^{-1}.

Semi-empirical and ab initio *MO Calculations.*—Tables 1 and 2 also summarize the results obtained from calculations carried out * at a semi-empirical level in the CNDO/2 [23] and PCILO approximations. The geometrical parameters employed, which were maintained constant for the formyl and acetyl groups, are the following (Å): C=O, 1.22; C–H, 1.088; C–C(exocyclic), 1.458; C–CH_3, 1.515; bond angles were chosen, as perfectly trigonal. For the remaining parts of the

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* All calculations were carried out on a Cyber 76 CDC computer.

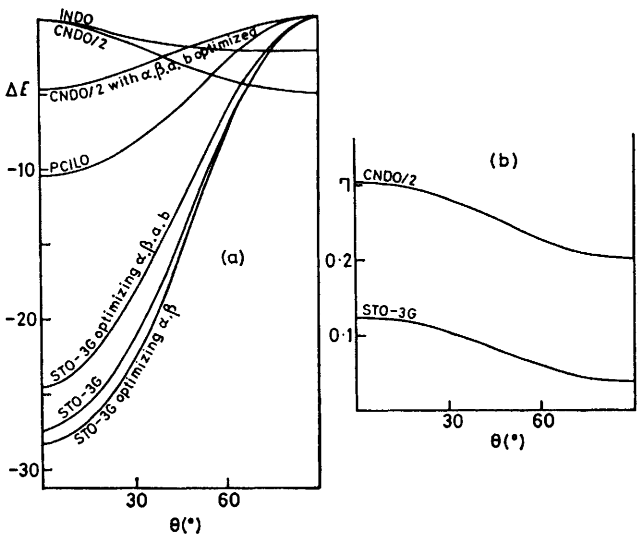

FIGURE 1 Behaviour of the total energy (a) and π-bond order (b) relative to the C–C bond joining the carbonyl group to the benzene ring in benzaldehyde, determined by semi-empirical and *ab initio* MO methods as a function of the angle of rotation of the formyl group (planar conformation corresponds to $\theta = 0°$)

molecules, a regular hexagon was chosen for the benzene ring with a C–C bond distance of 1.4 Å while heterorings were constructed from experimental geometries selected from the literature.[27]

Examples of the effect of rotation on the calculated total energy are reported in Figures 1 and 2 for benzaldehyde and acrylaldehyde. The zero-energy has been arbitrarily assigned to the conformation having the maximum calculated energy value and differs in the different MO approximations employed. For benzaldehyde, the rotational curves reported in Figure 1 show that PCILO predicts the correct stability order of

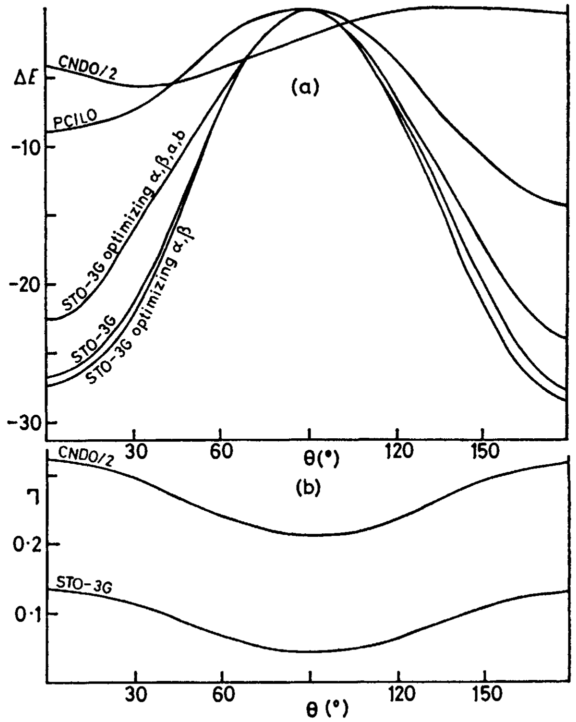

FIGURE 2 Behaviour of the total energy (a) and π-bond order (b) relative to the C–C bond joining the carbonyl to the vinyl group in acrylaldehyde determined by semi-empirical and *ab initio* MO methods as a function of the angle of rotation of the formyl group (planar conformation corresponds to $\theta = 0°$)

TABLE 2

Experimental free energy of activation (ΔG^*), calculated energy of activation (ΔE^*), experimental free energy differences (ΔG^0),[a] and calculated energy differences (ΔE^0)[a] between conformational isomers in acetyl derivatives (all values in kJ mol^{-1})

		Experimental		PCILO		CNDO/2		*ab initio* STO-3G	
No.	Molecule	ΔG^*	ΔG^0	ΔE^*	ΔE^0	ΔE^*	ΔE^0	ΔE^*	ΔE^0
(1′)	Acetophenone	22.4 [b]	0	8.63 min 0°	0	11.74 min 90°	0	18.30 min 0°	0
(2′)	*p*-Methoxy-acetophenone	28.1 [b] 27.6 [c]	0	8.84 min 0° and 180°	0.01 [d] (*anti* ≥ *syn*)	6.95 min 90°	0.08 [d] (*anti* ≥ *syn*)		
(3′)	*p*-Dimethylamino-acetophenone	34.2 [c]	0	8.80 min 0°	0	5.15 min 90°	0		
(4′)	*N*-Acetylpyrrole	50.81 [e] 54.0 [f] 54.4 [g]	0	52.32 min 0°	0	24.56 min 0°	0	32.78 min 0°	0
(5′)	2-Acetylfuran	38.25 [h]	0	19.18 *syn*→*anti*	4.95 (*syn* > *anti*)	20.01 *anti*→*syn*	4.42 (*anti* > *syn*)	29.10 *anti*→*syn*	5.11 (*anti* > *syn*)
(6′)	3-Acetyl-*N*-methylpyrrole	39.55 [i]	2.09 [h] (*anti* > *syn*)	14.18 *anti*→*syn*	9.94 (*anti* > *syn*)	4.08 [j] min 30°	4.08 (*syn* > *anti*)		
(7′)	*p*-Fluoroacetophenone	24.7 [b]	0	8.64 min 0°	0	8.69 min 90°	0	19.67 min 0°	0
(8′)	*p*-Methyl-acetophenone	24.7 [b]	0	8.68 min 0°	0	9.64 min 90°	0	9.63 min 0°	0

[a] The values in parentheses refer to the relative isomer stability. [b] T. Drakenberg, J. M. Sommer, and R. Jost, *Org. Magnetic Resonance*, 1976, **8**, 579. [c] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1975, 443. [d] From calculations it appears that the *syn–anti* conformation of the OMe relative to the MeCO group gives different energy values: this is not evidenced by the experimental results. [e] K. I. Dahlquist and S. Forsen, *J. Phys. Chem.*, 1969, **73**, 4124. [f] J. Elguero, C. Marzin, and L. Pappalardo, *Bull. Soc. chim. France*, 1974, 1137. [g] T. Matsuo and H. Shosenji, *Chem. Comm.*, 1969, 501. [h] L. Arlinger, K. I. Dahlquist, and S. Forsen, *Acta Chem. Scand.*, 1970, **24**, 662. [i] M. C. Fourniè-Zaluski, C. Jaureguiberry, and B. Roques *Tetrahedron Letters*, 1973, 4177. [j] Differences between the maximum and the minimum energy value in the rotational curve, where 0° corresponds to the *syn*-conformation.

fundamental and transition states, while CNDO/2 and INDO behave wrongly. In the case of acrylaldehyde (Figure 2) PCILO describes a situation where the *s-cis*(*syn*) and *s-trans*(*anti*) planar conformers are in the minima while the transition state should be approximately the perpendicular conformation. For this molecule the CNDO/2 total energy has a minimum at 45°, near the *s-cis* conformation. For other systems, such as furan-2-carbaldehyde and *N*-methylpyrrole-2-carbaldehyde, both CNDO/2 and PCILO indicate as more stable the planar rather than the perpendicular conformation. As a preliminary conclusion it seems, therefore, that both the presence of *ortho*-hydrogen atoms (as for benzaldehyde) or the geminal proton (in acrylaldehyde) and the shape of the ring (if one compares benzaldehyde and furan-2-carbaldehyde) set different limits of application of the CNDO/2 method on the conformational study of conjugated aldehydes. This situation is even more critical for acetyl derivatives: here also the conformation of the hydrogen atoms in the methyl group has to be accurately chosen.

It does not, therefore, seem feasible to employ total energies given by CNDO/2 to discuss in general the rotational behaviour of conjugated aldehydes and acetyl derivatives. This conclusion thus advances a criticism even against those cases where agreement with the experimental results is found since, on the basis of the large number of examples here reported, this agreement cannot be expected with certainty.

Previously we have found [26] that in dimethylamino derivatives of aromatic compounds the calculated energy differences between transition and ground planar states predicted by CNDO/2 are, for a large number of derivatives, smaller but roughly proportional to the experimental free energies of activation. In the case of conjugated aldehydes and ketones it seems that a similar conclusion cannot be drawn. The situation seems more promising for the energies obtained from PCILO, since the expected trend of stability for ground and transition states is predicted for all the compounds examined. The calculated energy differences between fundamental and transition state, ΔE^*, are noticeably lower than the experimental ΔG^* values but almost linearly dependent. The most significant deviations are given by compounds (13)—(15) and (4′), where rotation occurs around an N–C bond and not around the C–C bond as in the remaining molecules.

Energy calculations were also performed, for a certain number of molecules, by employing an *ab initio* procedure [21] and the minimal basis set STO-3G. The order of stability of ground and transition states is well reproduced for the compounds examined. The sequence of conformer stability is predicted in the correct order for compound (4) when referred to the experimental gas-phase situation.[4] For the other cases tackled by this approach, the experimental situation relative to the gas phase is not known, and the comparison with experimental results, as can be deduced from Table 1, reveals an apparent agreement only for compound (3).

It should, however, be pointed out that although the *ab initio* calculated ΔE^* values are quantitatively higher than those given by PCILO, they show no proportionality with the experimental ΔG^* values; in fact these calculated quantities are almost constant, ranging for the different molecules examined between 25 and 33 kJ mol^{-1}, while the corresponding experimental quantities range between 20 and 51 kJ mol^{-1}. When the analysis is extended to a number of molecules of the same class of compound and not restricted to a single example it seems therefore that quantitative predictions of barrier energies and conformer stabilities are rather problematic even in the *ab initio* framework, at least in the minimal basis set approach.

To analyse better the energy pattern given by the methods here employed, especially PCILO and *ab initio*, and to remove some difficulties raised in comparing experimental energies obtained in solution (and in different solvents) and calculated values, an attempt was made uniformly to refer the values to the gas phase by employing an empirical procedure suggested by Abraham.[4] By correlating the values of ΔE^* corrected for the gas phase with those calculated in the PCILO and *ab initio* schemes, no improvement is found with respect to the situation when the values obtained experimentally in solution are employed. For compounds (5), (10), and (12) the relative isomer stability in the gas phase is reversed with respect to that in solution, as already found for furan-2-carbaldehyde.[4] For compounds (5) and (12) the isomer stability in the gas phase coincides with that predicted by CNDO/2, PCILO, and *ab initio* STO-3G methods; for compound (10), for which calculations were carried out only for the CNDO/2 and PCILO methods, the gas-phase situation is in the opposite direction when compared with calculated stabilities. We thus see that all the relative stabilities of isomers calculated in the STO-3G scheme agree with the 'experimental' trend referred to the gas phase. Even if the agreement is perhaps fortuitous, it is not obtained on the same large scale with semi-empirical results.

In a previous paper [26] we pointed out that in dimethylamino derivatives of aromatic compounds the π-bond order of the exocyclic C–N bond given by CNDO/2 for all-planar molecules and the experimental ΔG^* values are linearly correlated. For the carbonyl compounds here examined, the π-bond orders relative to the exocyclic C–C bond evaluated by CNDO/2 in the planar conformations are also linearly correlated with the corresponding ΔG^* values and the equation obtained by a least-squares treatment is (1) where η is the π-bond order and the

$$\Delta G^* = 494.85\eta - 117.91 \qquad (1)$$

Bravais–Pearson coefficient is 0.930 7. The point relative to compound (15) deviates appreciably from the correlating line but rotation in this molecule occurs around a C–N bond: probably even for compounds (13) and (14) agreement is fortuitous. For compounds (3) and (7) probably better agreement could be expected if the experimental ΔG^* could be obtained as for the other compounds by employing the n.m.r. method.

The π-bond orders given by the *ab initio* STO-3G method, although calculated for a small number of molecules, still correlate with experimental ΔG^* values and the correlation is not worse than that obtained by employing the CNDO/2 results. These findings suggest that although the CNDO/2 method fails to give an appropriate description of the energy as a function of rotation, it provides a reasonable electronic description as shown also by the trend of calculated[28] dipole moments which are close to the experimental values. In many respects, owing to the particular parametrization chosen, this method seems to afford in general better quantitative calculated dipole moments when compared with *ab initio* methods, at least when minimal basis sets are employed.[29]

For compound (3) the energy calculation was also performed in the *ab initio* framework by introducing the more expanded 4–31G basis: the order of isomer stability (*syn* > *anti*) is wrongly predicted and the energy of activation calculated for the *syn* ⟶ *anti* (33.56 kJ mol^{-1}) process is higher than the experimental value.

Effect of Molecular Geometry on MO Results.—To check the effect of molecular geometry, energy calculations in the *ab initio* scheme were also performed by allowing optimization of a number of bond lengths and angles relative to the formyl group. This was done first in the minimal STO-3G basis set approach allowing for the optimization of the angles α and β. We found thus for compound (3) that the angles α and β from the initial 120° for both planar isomers, change to α_{syn} 116.33 and α_{anti} 115.61° and to β_{syn} 122.16 and β_{anti} 122.01°, showing that the angle α reaches final values considerably different from those of the standard geometry. Correspondingly no large changes are found in calculated energies, as can be seen in Table 3, and the correct *anti* > *syn* stability order is maintained. When optimization is performed with the 4–31G basis set the best values become α_{syn} 117.43, α_{anti} 117.18, β_{syn} 122.52, and β_{anti} 122.40°, not far from those given by the smaller basis set. The final energy values are somewhat different (33.97 for the *syn* ⟶ *anti* and 38.12 kJ mol^{-1} for the *anti* ⟶ *syn* process) and the activation energy is once more higher than the experimental value, the order of isomer stability is preserved. When the bond lengths a and b are also allowed to change, the STO-3G basis yields an optimum value of 1.50 Å for a, quite different from the initial 1.45 Å, for both planar isomers and of 1.52 Å for the perpendicular conformation, while b does not change appreciably from 1.22 Å: the angles α and β are now α_{syn} 115.2, α_{anti} 114.3, β_{syn} 123.1, and β_{anti} 123.7°. The changes in calculated energy by performing optimization also of the bond lengths with respect to the results obtained with the initial geometrical parameters or by modifying only the α and β angles, are significant, especially for the perpendicular conformation, and the resulting activation energy, as shown in Table 3, becomes closer to the experimental value. By employing the four parameters optimized in the STO-3G basis set and the larger 4–31G basis set, the calculated value of the activation energy exceeds the experimental value (32.18 for the *syn* ⟶ *anti* and 35.08 kJ mol^{-1} for the *anti* ⟶ *syn* process). Application of the 4–31G basis set approach to the other molecules here considered becomes problematic owing to their large dimensions.

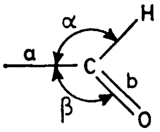

TABLE 3

Calculated energies of activation (kJ mol^{-1}) for a number of aldehydes in the *ab initio* and semi-empirical CNDO/2 MO schemes in relation also to changes in geometrical parameters

Compound	STO-3G	STO-3G α, β optimized	STO-3G a, b, α, β optimized	CNDO/2 with a, b, α, β optimized in the STO-3G approach
(1)	27.46	28.70	24.46	4.67
(2)				6.46
(3) *syn*→*anti*	26.63	27.09	22.69	
anti→*syn*	27.66	28.51	24.05	
(4) *syn*→*anti*	27.87	28.34	23.76	28.68
anti→*syn*	31.51	32.02	27.52	30.37
(5) *syn*→*anti*				28.27
anti→*syn*				22.00
(6)				0.97
(9) *syn*→*anti*				3.53
anti→*syn*				3.44
(10) *syn*→*anti*				6.53
anti→*syn*				6.83
(11) *syn*→*anti*				6.69
anti→*syn*				8.72
(12) *syn*→*anti*				3.38
anti→*syn*				3.56

It thus appears that the standard geometry employed in our energy calculations differs, especially as regards the exocyclic C–C bond, labelled a, from the best molecular arrangement which gives energy minima in the *ab initio* calculations. Since the results of the CNDO/2 semi-empirical method are, for most of the molecules here examined, not in line with experimental results, the energies for a number of conformations have been calculated with the a, b, α, and β parameters optimized in the *ab initio* STO-3G. The results indicate qualitatively correct behaviour, with the energy minimum corresponding to the planar conformation, as shown in Figure 1 for benzaldehyde. Incidentally we observe that the total energy of the molecule is higher than the value found when standard bonds and angles are employed: as regards bond length a, the value which leads to a minimum in the total energy is *ca.* 1.45 Å, a value corresponding again to an incorrect conformational behaviour with the perpendicular more stable than the planar state. The geometrical parameters thus seem not to be a limitation in the calculation of total energy with the semi-empirical CNDO/2 method: in particular, the values of the π-bond order obtained with the optimized parameters still fit an approximately linear correlation with the experimental activation free energies. The behaviour of the energy as a function of conformational change of the carbonyl group is thus substantially incorrect when given by the CNDO/2 approximation: the requirements of a short C–C bond length (parameter a) for a stable molecule (but this does not agree with the planar being more stable than the perpendicular conformation) could suggest that an inappropriate balancing of bonding terms and repulsive interactions is carried out by the method in the evaluation of the total energy.

Factorization of the CNDO/2 Energy.—To analyse this aspect more deeply we made an attempt to study separately the energy components obtained by factorization of the total energy for different conformations. Fundamentally we have separated the total energy for different conformations into two components, namely one- and two-centre terms, according to a procedure suggested by Gordon.[30] The one-centre term, $\Sigma\Delta E_A$, is the change in energy of the atoms A as a function of internal rotation, while the terms ΔE_{AB} represent two-atom energy contributions to the barrier from bonded, $E_{AB}{}^{b}$, and non-bonded $E_{AB}{}^{n}$ atoms. The term E_{AB} is further factorizable in three contributions, namely $E_{AB}{}^{(1)}$, $E_{AB}{}^{(2)}$, and $E_{AB}{}^{(3)}$ representing respectively the bonding contribution between orbitals on atoms A and B, the contribution of exchange interactions, and finally the electrostatic interaction between A and B. The separate behaviour of the terms ΣE_A, $\Sigma E_{AB}{}^{(1)}$, $\Sigma E_{AB}{}^{(2)}$, $\Sigma E_{AB}{}^{(3)}$, and ΣE_{AB} has been studied for a number of the molecules here examined, but we discuss only the effect of rotation on these terms for compounds (1) and (4), since the calculated energy for these compounds is opposite.

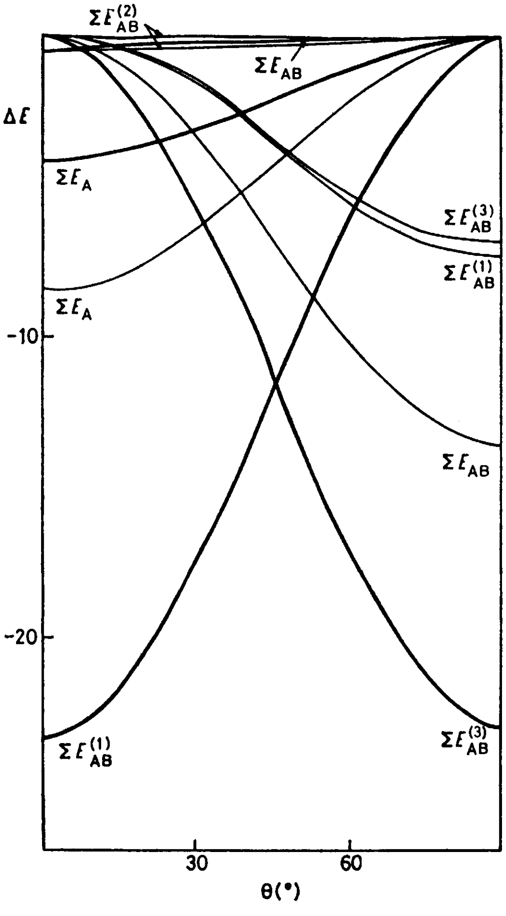

FIGURE 3 Factorization of the contributions to the energy barrier calculated by CNDO/2 in benzaldehyde. The explanation of the single terms may be found in the text. The lines marked more heavily refer to the calculation employing the geometrical parameters a, b, α, and β obtained by optimization in the *ab initio* STO-3G and those marked less heavily to the calculation employing standard geometries (C–C bond length 1.46 Å, angles 120°)

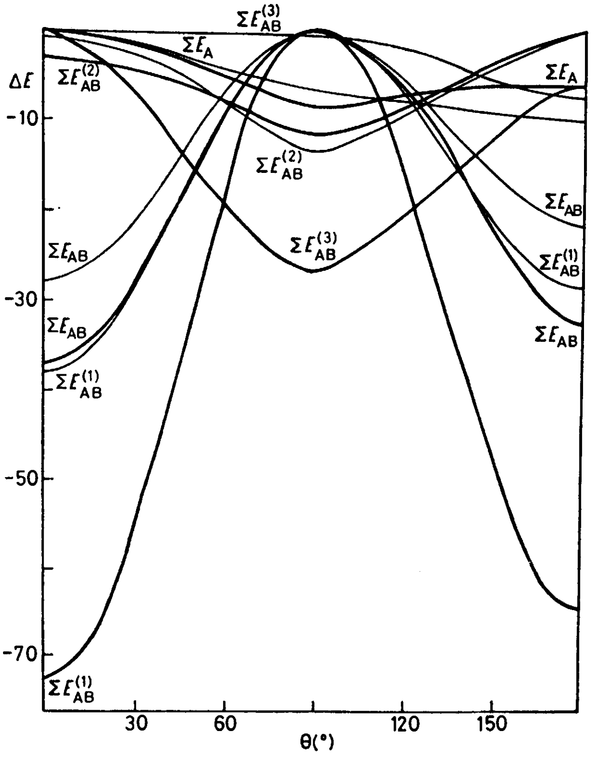

FIGURE 4 Behaviour on internal rotation of the terms contributing to the total molecular energy calculated by the CNDO/2 method for furan-2-carbaldehyde. The explanation of the single terms may be found in the text. The lines marked more heavily refer to the calculation employing the geometrical parameters a, b, α, and β obtained by optimization in the *ab initio* STO-3G and those marked less heavily to the calculation employing standard geometries

For compound (1), by employing a C–C bond distance a of 1.46 Å, which predicts an incorrect behaviour of the energy barrier, the single terms give the patterns reported in Figure 3 (lines marked less heavily). A relevant point of these diagrams is that the terms $\Sigma\Delta E_{AB}{}^{(1)}$ and $\Sigma\Delta E_{AB}{}^{(3)}$ contribute both to a more stable perpendicular conformation. For the $\Sigma\Delta E_{AB}{}^{(1)}$ term this is unexpected, since bonding between orbitals in a conjugated system, according to current theories of chemical bonding, should be higher in the planar conformation. Further, by examining the contribution of any single pair of atoms to ΣE_{AB} and to the single two-term factors, it is found that the contributions from pairs of non-bonded atoms, especially the two *ortho*-hydrogen atoms, are almost insignificant. This fact indicates that the failure to predict the correct behaviour of energy barriers in conjugated carbonyl compounds should depend on an incoherent composition of bonding effects rather than on an overestimate of repulsive interactions.

When a longer C–C bond length is employed, *i.e.* that given by the *ab initio* STO-3G energy minimization, the behaviour of the single terms changes consistently, as illustrated in Figure 3 (lines marked more heavily). The terms $\Sigma E_{AB}^{(1)}$ and $\Sigma E_{AB}^{(3)}$ behave now in the opposite sense on rotation of the formyl group, with $\Sigma E_{AB}^{(1)}$ now contributing in stabilizing the planar conformation.

In the case of compound (4) CNDO/2 predicts correctly the transition state corresponding energetically to the perpendicular conformation. By employing two different values for the C–C bond length as in the case of compound (1), the behaviour on rotation of the terms contributing to the total energy is qualitatively similar. The ΣE_{AB} and $\Sigma E_{AB}^{(1)}$ terms show the minimum in the planar conformation (Figure 4), while the reverse situation is found for $\Sigma E_{AB}^{(2)}$ and $\Sigma E_{AB}^{(3)}$. Very small contributions are found for the separate terms corresponding to pairs of non-bonded atoms as found for compound (1).

It seems thus that the improper behaviour of the CNDO/2 energy on rotating the carbonyl group in conjugated systems originates mainly from the $E_{AB}^{(1)}$ terms, which seem to be greatly underestimated for planar conformations with respect to the other terms.

For compounds (1) and (4) geometry optimization by searching for a minimum in the CNDO/2 total energy was also performed, by a known method.[31] The planar conformation of both compounds shows an optimum bond length a of 1.44 Å, considerably shorter than that required by the *ab initio* energy minimum, while for the carbonyl C–O bond a higher value is required, 1.26 Å. Smaller differences are found as regards the remaining bond distances and bond angles. The same qualitative result is found for the perpendicular conformation, which is wrongly predicted, for compound (1), as the ground state. From the analysis of the single terms in which can be factorized the total energy obtained for different values of the exocyclic C–C bond length it is clear that CNDO/2 underestimates the $E_{AB}^{(1)}$ term especially in the planar conformations, and short bond distances are required for providing values of this term which compensate the $E_{AB}^{(3)}$ (electrostatic repulsive) term giving a minimum in the total energy value.

Conclusions.—In conclusion, it is thus found that for conjugated aldehydes and ketones an analytical prediction of the rotational internal behaviour in energy terms can be found safely only by employing *ab initio* procedures. The semi-empirical PCILO method seems to provide a correct qualitative prediction of the barriers, while for CNDO/2, analyses carried out on a large class of molecules seem to indicate that prediction of good rotational behaviour in one conjugated aldehyde or ketone should be considered fortuitous. On the other hand the excellent electronic distribution given by this method allows an analysis of the barrier to internal rotation of the formyl and acetyl groups. In fact the good linear correlation between π-bond order and experimental free energy of activation shows that the stability of the ground state, related to the degree of conjugation between the carbonyl group and the unsaturated system, is a factor which largely determines the size of the energy barriers. This fact, which has been found also [26] for conjugated dimethylamino derivatives, may provide, through empirical correlations, a useful way of predicting quantitatively the size of barriers to internal rotation.

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