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Molecular Orbital Calculations of Rotational Strengths: A Study of Skewed Diketones

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A skewed glyoxal molecule is considered as a model for the study of the optical activity of α-diketones. The rotational strengths are calculated for various angles of twist, between trans ($\vartheta = 0°$) and *cis* ($\vartheta = 180°$). The wavefunctions are computed both by the extended Hückel method and by the SCF-CNDO method, considering all 22 valence electrons. The effect of configuration interaction is studied. All two-center terms are included in the calculation of the electric and magnetic transition moments. The results predict the rotational strength of the lowest transition to be negative for $0° < \vartheta < 90°$ when the molecule is twisted in a right-handed way and to be positive for $90° < \vartheta < 180°$. In general, the lowest transition is followed by a transition with opposite rotational strength, in analogy to the predictions of a simple exciton model.

Ein aus der ebenen Lage gedrehtes Glyoxalmolekül wird als Modell zum Studium der optischen Aktivität von α-Diketonen betrachtet. Die Rotationsstärken werden für verschiedene Drehwinkel ermittelt, zwischen *trans* ($\vartheta = 0°$) und *cis* ($\vartheta = 180°$). Die Berechnung der Wellenfunktionen erfolgt sowohl nach der erweiterten Hückelmethode als auch nach dem SCF-CNDO-Verfahren, unter Berücksichtigung aller 22 Valenzelektronen. Der Einfluß der Konfigurationswechselwirkung wird studiert. Die Berechnung der elektrischen und magnetischen Übergangsmomente schließt alle Zweizentren-Beiträge ein. Die Resultate zeigen, daß die Rotationsstärke des langwelligsten Übergangs im Falle eines rechtsgedrehten Moleküls negativ ist für $0° < \vartheta < 90°$ und positiv für $90° < \vartheta < 180°$. Im allgemeinen wird der langwelligste Übergang von einem Übergang mit entgegengesetzter Rotationsstärke gefolgt, in Analogie zu den Voraussagen eines einfachen Exziton-Modells.

Une molécule de glyoxale non-plane est considérée comme modèle pour l'étude de l'activité optique de α-dicétones. Les forces rotatoires sont calculées pour différents angles de torsion, entre la position *trans* ($\vartheta = 0°$) et *cis* ($\vartheta = 180°$). Les fonctions d'onde sont calculées par les méthodes "extended Hückel", ainsi que "SCF-CNDO", en considérant les 22 electrons de valence. L'effet de l'interaction de configurations est étudié. Tous les termes bicentriques sont inclus dans le calcul des moments de transition électriques et magnétiques. Les résultats montrent que la force rotatoire de la transition de plus basse fréquence est négative pour $0° < \vartheta < 90°$ dans une molécule tournée en sens droit et positive pour $90° < \vartheta < 180°$. En général, la transition de plus basse fréquence est suivie d'une transition dont la force rotatoire est opposée, en analogie aux prédictions d'un simple modèle exciton.

Introduction

Historically, the molecular orbital theory of optical activity has grown out of the "one electron theory" [1, 2]. Attention was focused on a certain part of a molecule, or chromophore, within which relevant electronic transitions were assumed to be localized. The asymmetric environment of the chromophore was treated as a perturbation. A limited MO description of the perturbed chromophore served as basis for the calculation of rotational strengths. This approach proved fruitful for saturated ketones and led to the familiar sector rules [2–6]. However, it was of more limited use in the study of "inherently dissymmetric" larger systems, such as unsaturated ketones, α- and β-diketones or skewed dienes, which called for a more comprehensive MO description [7, 8]. Recent advances, aided by the use of computers, have now made it possible to obtain approximate molecular orbitals extending over all atomic centers of relatively large molecules and taking into account all valence electrons. An optically active molecule may thereby always be treated as "inherently dissymmetric". In this sense quite a few investigations have already been carried out [9–12]. Within such calculations many new problems arise, and two questions seem to be of immediate importance. The first question concerns the contribution of the numerous interatomic terms to the values of the electric dipole and magnetic dipole transition moments. It appears that in calculations invoking the zero differential overlap approximation such two-center terms may, at least, partly, be neglected [13]. In general, this assumption may, however, scarcely be justified. The second question is a much more difficult and fundamental one. It pertains to the influence of configuration interaction, not merely on the magnitude, but possibly even on the sign of the rotational strengths. For it appears that the rotational strength may be very sensitive to configurational mixing.

In the present note we consider from this point of view the simplest possible dicarbonyl compound, glyoxal. The molecule is "twisted" from the trans conformation ($\vartheta = 0°$) to the cis conformation ($\vartheta = 180°$) and the rotational strengths are computed at various intermediate angles. Different types of wavefunctions are used: a) Extended Hückel molecular orbitals, b) Wavefunctions of the SCF-CNDO type, with and without the interaction of singly excited configurations. By increasing the carbon-carbon distance for a given angle of twist ($\vartheta = 135°$) the fading interaction of the two carbonyl groups is also studied.

The Calculation of Rotational Strengths

All molecular orbitals used in this investigation are expressed in terms of 1*s*, 2*s*, 2*p* Slater atomic orbitals. Therefore a FORTRAN program was written to calculate the matrix elements of the operators ∇ and $\boldsymbol{r} \times \nabla$ in such a basis. Electric transition moments are calculated in the dipole velocity form. While the operator ∇ is independent of origin, the operator $\boldsymbol{r} \times \nabla$ is not. If $\chi_{q'}$ and χ_q define atomic orbitals centered on atoms q′ and q we find in general:

$$\langle \chi_{q'} | \boldsymbol{r} \times \nabla | \chi_q \rangle = \boldsymbol{r}_{oq} \times \langle \chi_{q'} | \nabla | \chi_q \rangle + \langle \chi_{q'} | \boldsymbol{r}^{(q)} \times \nabla | \chi_q \rangle ,$$

$$\boldsymbol{r}_{oq} = X_q \boldsymbol{i} + Y_q \boldsymbol{j} + Z_q \boldsymbol{k} .$$

X_q, Y_q and Z_q are the coordinates of atom q in a general molecular frame of reference, $\boldsymbol{r}^{(q)}$ designates the position vector with respect to the center of atom q.

The computation of two-center integrals must be carried out in an internal coordinate system *x*, *y*, *z* for each atom q′ and q, in which one axis, *z* say, coincides with the lines joining the two centers. One then finds in the most straightforward way:

$$\langle s_{q'}|\,\nabla|s_q\rangle = \boldsymbol{z}\langle s_{q'}|\frac{\partial}{\partial z}|s_q\rangle\,,$$

$$\langle s_{q'}|\,\nabla|p_q\rangle = \boldsymbol{x}n_{xq}\langle s_{q'}|\frac{\partial}{\partial x}|p_{xq}\rangle$$

$$+\,\boldsymbol{y}n_{yq}\langle s_{q'}|\frac{\partial}{\partial y}|p_{yq}\rangle + \boldsymbol{z}n_{zq}\langle s_{q'}|\frac{\partial}{\partial z}|p_{zq}\rangle\,,\quad \text{etc.,}$$

where $\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$ are unit vectors in the directions of x, y, z, and p_x, p_y, p_z are p-functions defined in the internal coordinate system. The direction cosines of any given p-function on q, p_q, with respect to x, y, z are designated by n_{xq}, n_{yq}, n_{zq}. From the vector components of ∇ in the internal coordinate system the respective components in the general $\boldsymbol{i}$-, $\boldsymbol{j}$-, $\boldsymbol{k}$-frame may easily be calculated.

Concerning the numeric evaluation of the dipole velocity integrals, the operators $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$ acting on Slater functions give linear combinations of other Slater functions. Thus all the dipole velocity integrals may be expanded in terms of overlap integrals and evaluated as indicated by Lofthus [14].

The rotational strength $R_{i\to j}$ for a transition between states i and j is obtained by the relation

$$(E_j - E_i)R_{i\to j} = -\frac{e^2\hbar^3}{2m^2c}\langle i|\,\nabla|j\rangle\langle j|\boldsymbol{r}\times\nabla|i\rangle\,.$$

If the value of the integral $\langle i|\,\nabla|j\rangle$ is inserted in atomic units, we must yet divide the right-hand side by a_0, the Bohr radius. We then find $e^2\hbar^3/2m^2ca_0 = 1.027\times 10^{-48}$ in cgs units. If $R_{i\to j}$ itself is to be obtained in cgs units, $(E_j - E_i)$ must of course be expressed in ergs.

Calculations on Glyoxal

Table 1 gives the matrix elements of the $\boldsymbol{k}$-component of the operator $\boldsymbol{r}\times\nabla$ in the Slater atomic orbital basis for glyoxal twisted at an angle $\vartheta = 45°$. It serves to show the great number of interatomic terms and the relatively large values of some of them. It may also be used as a numeric check for other investigators performing similar calculations. The atomic coordinates and Slater exponents are given in Table 2.

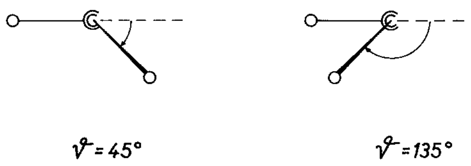

Fig. 1. The definition of the angle ϑ. The C–O bond which is closer to the observer is rotated to the right (clock-wise)

Table 1. *Matrix elements of the* **k***-component of the operator* $\mathbf{r} \times \nabla$ *in the Slater atomic orbital basis, for glyoxal twisted at an angle of* $\vartheta = 45°$

	Hydrogen 1	Hydrogen 2		Carbon 1				Carbon 2				Oxygen 1				Oxygen 2		
	1s	1s	2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	2py	$2p_z$
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	0.0																	
2	0.0	0.0																
3	0.3403	−0.0475	0.0															
4	0.6194	0.0173	0.0	0.0														
5	−0.2196	0.0969	−0.6737	−1.0000	0.0													
6	−0.1513	0.0112	0.0	0.0	0.0	0.0												
7	−0.0475	0.3403	0.0	0.0	−0.1861	0.0	0.0											
8	−0.0173	−0.6194	0.0	0.0	−0.0658	0.0	0.0	0.0										
9	−0.0969	0.2196	−0.1861	0.0658	0.0	0.0	0.6737	−1.0000	0.0									
10	0.0112	−0.1513	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0								
11	0.1668	−0.0285	0.2930	0.5630	0.0512	0.1584	−0.0258	−0.0165	0.0516	−0.0081	0.0							
12	0.0170	0.0288	−0.1534	−0.1542	0.2018	−0.1182	0.0294	0.0163	−0.0522	0.0109	−1.3204	0.0						
13	0.1457	0.0049	0.0869	0.2796	0.3799	0.0988	−0.0017	−0.0042	0.0116	−0.0013	−1.7746	−1.0000	0.0					
14	−0.0785	0.0099	−0.1010	−0.2427	0.0204	0.1368	0.0059	0.0052	−0.0129	−0.0075	0.0	0.0	0.0	0.0				
15	−0.0285	0.1668	−0.0258	0.0165	−0.0516	−0.0081	0.2930	−0.5630	−0.0512	0.1584	0.0	−0.0002	−0.0002	0.0	0.0			
16	−0.0288	−0.0170	−0.0294	0.0163	−0.0522	−0.0109	0.1534	−0.1542	0.2018	0.1182	−0.0002	0.0000	−0.0004	0.0	1.3204	0.0		
17	−0.0049	−0.1457	0.0017	−0.0042	0.0116	0.0013	−0.0869	0.2796	0.3799	−0.0988	−0.0002	0.0004	−0.0000	0.0	1.7746	−1.0000	0.0	
18	0.0099	−0.0785	0.0059	−0.0052	0.0129	−0.0075	−0.1010	0.2427	−0.0204	0.1368	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 2. *Coordinates and Extended Hückel parameters for glyoxal,* $\vartheta = 45°$

Atom	Coordinates in Å			Slater exponent	Ionization potentials			
	x	y	z	k	[eV]			
H 1	1.305	0.872	−0.361	1.200	1s	−13.6		
H 2	−1.305	−0.872	−0.361	1.200		−13.6		
C 1	0.76	0.0	0.0	1.625	2s	−21.4	2p	−11.4
C 2	−0.76	0.0	0.0	1.625		−21.4		−11.4
O 1	1.43	−1.064	0.441	2.275		−35.3		−17.3
O 2	−1.43	1.064	0.441	2.275		−35.3		−17.3

Table 3. *Extended Hückel energies in eV and rotational strengths in cgs units of twisted glyoxal*

angle ϑ	$a \to a$		$a \to b$		$b \to a$		$b \to b$	
	ΔE (eV)	$R \cdot 10^{40}$ (cgs)	ΔE	$R \cdot 10^{40}$	ΔE	$R \cdot 10^{40}$	ΔE	$R \cdot 10^{40}$
0°	2.02	0.0	8.09	0.0	4.73	0.0	10.80	0.0
22.5°	2.23	−18.1	7.79	3.4	4.95	18.6	10.52	6.0
45°	2.81	−28.6	7.00	10.6	5.55	27.4	9.74	11.3
67.5°	3.68	−32.8	5.92	20.2	6.44	28.2	8.67	15.3
90°	4.76	−33.4	4.77	30.0	7.49	25.6	7.50	17.7
112.5°	5.94	−31.0	3.72	38.4	8.58	21.6	6.36	17.9
135°	7.06	−25.0	2.87	41.5	9.57	16.1	5.38	15.1
157.5°	7.90	−14.3	2.32	30.3	10.27	8.9	4.69	8.9
180°	8.22	0.0	2.13	0.0	10.52	0.0	4.43	0.0

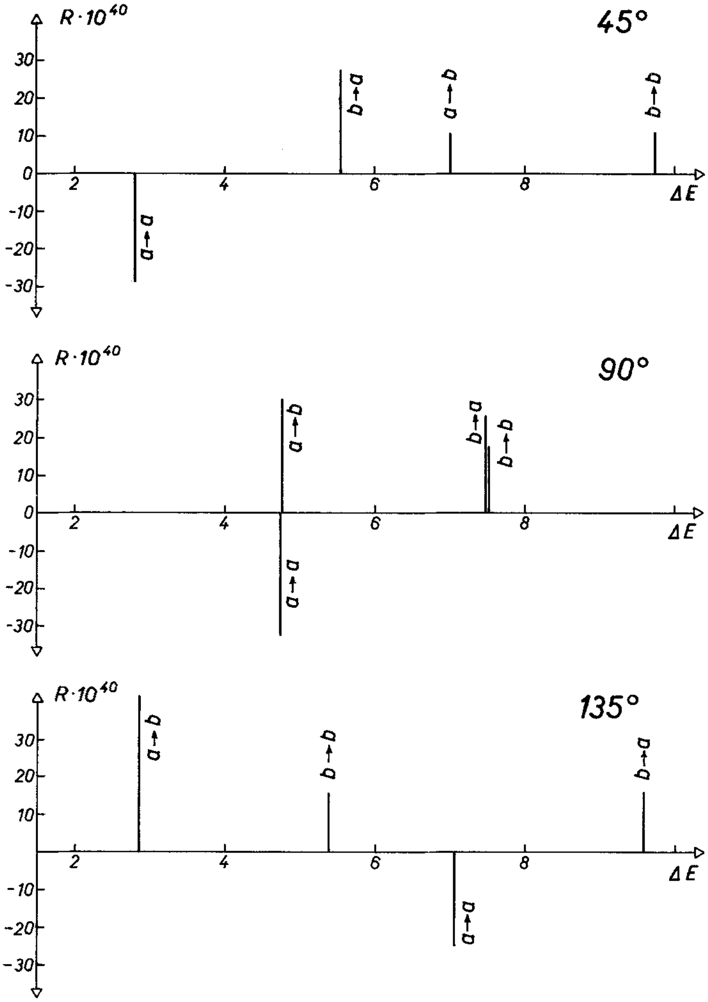

Fig. 2. Transition energies and rotational strengths for the angles $\vartheta = 45°, 90°, 135°$, as obtained from extended Hückel calculations (see also Table 3)

a) Extended Hückel Calculations. The diagonal elements of the Hückel matrix were set equal to valence state ionization potentials (Table 2), the non-diagonal elements were computed according to the formula:

$$H_{q'q} = (2.55 - |S_{q'q}|)\, S_{q'q}(H_{q'q'} + H_{qq})/2 .$$

Table 3 and Fig. 2 show computed transition energies and rotational strengths. All interatomic terms have been included in the calculation of electric and magnetic transition moments. At every angle of twist the molecule maintains a twofold axis of symmetry, perpendicular to the C–C bond and bisecting the angle ϑ. Consequently, all orbitals may be characterized according to their transformation properties under C_2 by either a (symmetric) or b (antisymmetric). Only those four transitions are shown, which at some angle ϑ have either lowest or next to lowest energy. For instance, at $\vartheta = 45°$ the transition $a \rightarrow a$ has an energy of 2.81 eV and lies lowest, whereas at $\vartheta = 135°$ its energy increases to 7.06 eV, moving above the values for the $a \rightarrow b$ and $b \rightarrow b$ transitions. We then notice the following particular features: At an angle of 45° (close to the trans conformation) the rotational strength of the lowest transition ($a \rightarrow a$) is negative, whereas the other transitions show a positive rotational strength. At $\vartheta = 135°$ (close to the cis conformation) the transition of lowest energy ($a \rightarrow b$) is predicted to have a positive rotational strength, but there occurs at shorter wavelength the transition ($a \rightarrow a$) with negative rotational strength. Close to the angle $\vartheta = 90°$ a degeneracy appears and it seems that the rotational strengths of the $a \rightarrow a$ and $a \rightarrow b$ transitions almost cancel each other. The calculated energy of the lowest transition is, in its dependence on ϑ, in qualitative agreement with the spectroscopically observed trend for cyclic α-diketones [15].

b) SCF-CNDO *Calculations.* The general procedure follows the indications given in Ref. [16] and [17]. The detailed parametrization will be published as a separate investigation [18].

Table 4 and Fig. 3 show the results of calculations for the two lowest singlet excited states. The computations were performed both without and with the interaction of the forty lowest singly excited configurations. The molecular orbitals being normalized without overlap, it may appear justified to neglect two-center terms in the computation of the transition moments as well. We have nevertheless deemed it important to also include interatomic terms explicitly, using the same set of SCF MO's. (Although strictly speaking the orbitals should then be transformed so as to be normalized including overlap).

In all cases we notice a pattern similar to the one encountered in the Extended Hückel treatment: At angles below 90° the transition of lowest energy is of overall symmetry A ($a \times a$ and (or) $b \times b$) and the rotational strength is negative. At angles above 90° the lowest transition is of symmetry B ($a \times b$ and (or) $b \times a$) with a positive rotational strength. Close to 90° a degeneracy again appears, irrespective of the particular method of calculation, and a partial cancellation of opposite rotational strengths occurs. In general, the CNDO calculations seem to predict that the rotational strength of the next to lowest transition is opposite in sign and smaller than the one of the lowest transition.

Table 4. *Energies in eV and rotational strengths in* cgs *units of twisted glyoxal calculated by the* SCF-CNDO *method, without and with configuration interaction* (CI), *without and with the inclusion of interatomic terms* (IAT) *in the computation of the transition moments. In the first three rows the angle of twist is varied for fixed bond lengths. In the last two rows the* C–C *distance is increased for an angle of twist of* 135°

	no CI						with CI					
	Lowest singlet A			Lowest singlet B			Lowest singlet A			Lowest singlet B		
	ΔE	$R \cdot 10^{40}$		ΔE	$R \cdot 10^{40}$		ΔE	$R \cdot 10^{40}$		ΔE	$R \cdot 10^{40}$	
		no IAT	with IAT		no IAT	with IAT		no IAT	with IAT		no IAT	with IAT
45°	3.307	−22.7	−31.0	5.054	− 6.2	−21.2	2.595	−17.3	−24.1	3.447	+ 8.2	+ 3.8
90°	4.305	−21.4	−46.8	4.307	+33.9	+64.0	3.203	−13.9	−29.5	3.197	+29.3	+37.9
135°	4.877	− 3.3	+ 8.2	3.233	+32.2	+40.4	3.363	− 6.0	− 2.1	2.528	+27.1	+27.8
135° 2.0 Å	3.923	−35.7	−40.2	3.168	+44.3	+36.7	3.207	−25.8	−26.3	2.667	+40.2	+32.7
135° 3.0 Å	2.111	−66.5	−41.1	2.050	+68.6	+41.5	2.069	−68.9	−40.7	2.009	+71.2	+40.7

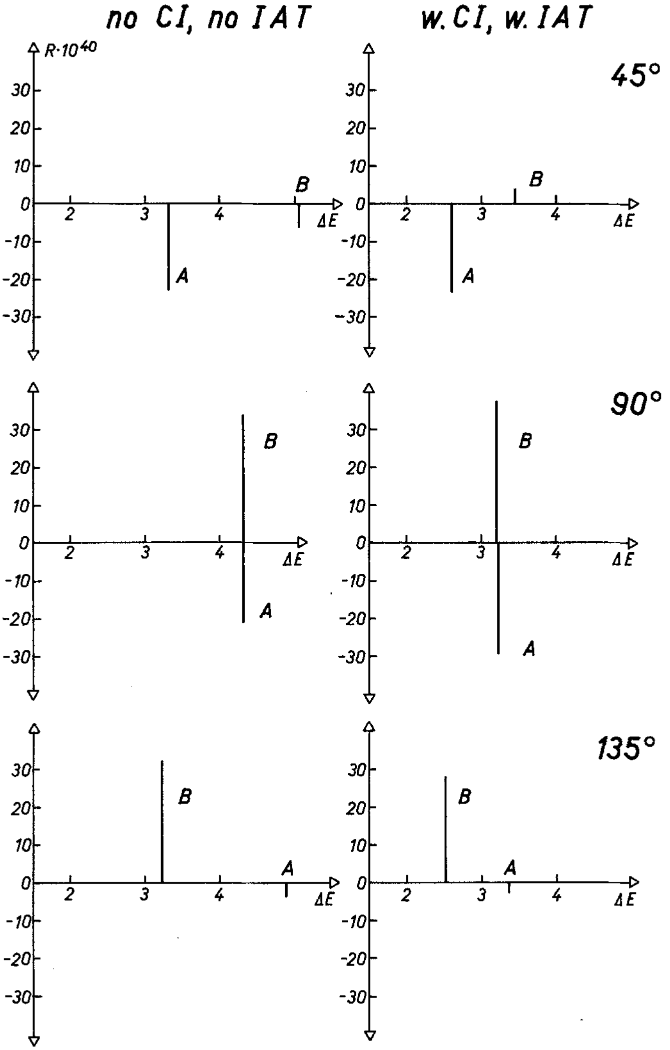

Fig. 3. Energies and rotational strengths of the two lowest transitions for the angle $\vartheta = 45^\circ, 90^\circ, 135^\circ$, as obtained from SCF-CNDO calculations (see also Table 4). Results at right are with configuration interaction and with the inclusion of interatomic terms in the computation of the transition moments

By increasing the C–C bond distance we may study the decreasing interaction of the two carbonyl groups. At a C–C distance of 3 Å we find the two transitions A and B (Fig. 4) to be nearly degenerate with opposite rotational strengths of about equal magnitude. In the language of molecular orbitals localized on the individual keto groups I and II these two transitions may be designated by $(n_{\mathrm{I}}+n_{\mathrm{II}})\rightarrow(\pi_{\mathrm{I}}^*+\pi_{\mathrm{II}}^*)$ and $(n_{\mathrm{I}}+n_{\mathrm{II}})\rightarrow(\pi_{\mathrm{I}}^*-\pi_{\mathrm{II}}^*)$ respectively. The localized transitions $n_{\mathrm{I}}\rightarrow\pi_{\mathrm{I}}^*$ and $n_{\mathrm{II}}\rightarrow\pi_{\mathrm{II}}^*$ both have negative rotational strengths.

The transition energies predicted by the calculations including configuration interaction are shifted somewhat too far to the red. Without configuration interaction the agreement with data on cyclic α diketones is better [15].

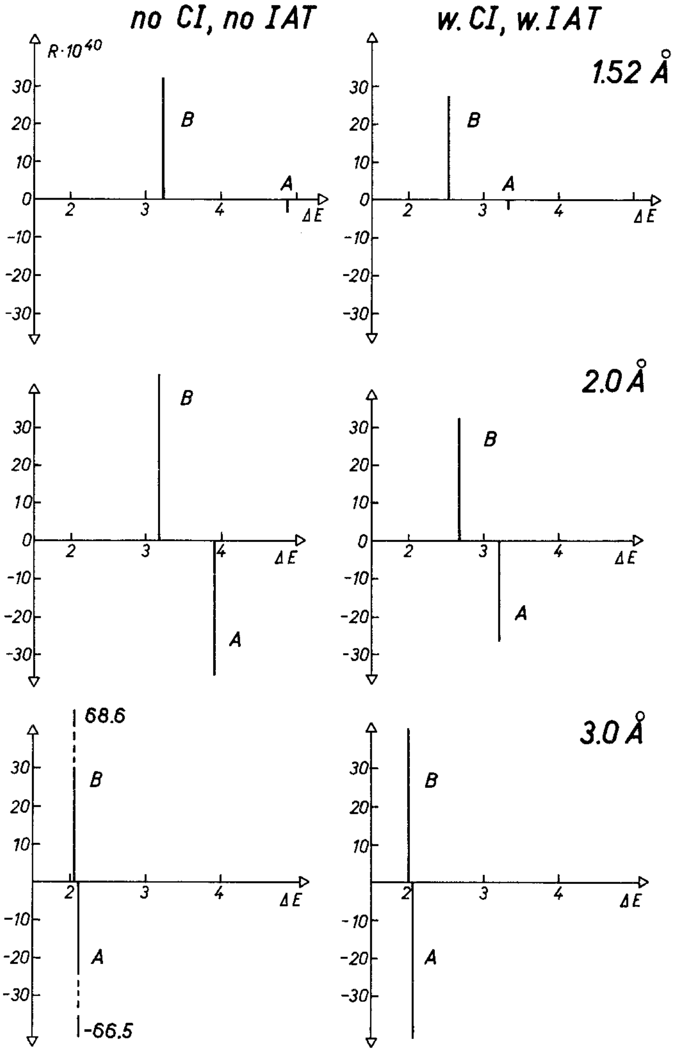

Fig. 4. Energies and rotational strengths of the two lowest transitions for varying C–C bond length at a fixed angle of $\vartheta = 135°$, as obtained from SCF-CNDO calculations (see also Table 4)

Conclusions

Preliminary calculations on α-cyclohexadione and comparison with the CD spectra of some 11,12-diketosteroids show that the sign of the rotational strengths of the two lowest transitions are mainly determined by the relative position of the two carbonyl groups. This allows us to believe that the twisted glyoxal model may be useful in making some predictions of general validity for α-diketones. If the diketone is twisted in a right-handed (see Fig. 1) sense, the rotational strength of the lowest transition should be negative for $0° < \vartheta < 90°$ and positive for $90° < \vartheta < 180°$. A change of sign occurs at or around 90°. These conclusions are supported by all calculations, irrespective of the adopted method. The predictions concerning the next to lowest transition are more sensitive to the particular approximations. In general it appears that the lowest transition is followed by a transition with opposite rotational strength. When using CNDO wavefunctions it does not seem unjustified to neglect two-center terms in the transition moments. One must however remember that this also implies neglecting all direct contributions from hydrogen atoms. In the present case this is of negligible importance, but may play a role in larger molecules.

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