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Multi-Conformational Compounds with Two Absorbing Groups

III. The Non-Planar Phenyl-Ketone System

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A configurational-interaction scheme is used to study the series of conformers of the C_6H_5—C = O ("phenyl-carbonyl") structure. The dependence on the dihedral C_6H_5—CO angle of electronic state-energies and oscillator-strengths is obtained and compared with data concerning the series of benzocyclenones. The relation between physical data, on the one hand, dihedral angle and ring flexibility, on the other, is discussed.

Verschiedene Konformere des Phenyl-Carbonyl-Gerüsts werden mit einer Konfigurationen-wechselwirkungsmethode untersucht. Die Abhängigkeit der elektronischen Energieniveaus und der Energien und Oszillatorenstärken von dem φ-CO-Diederwinkel wird mit experimentellen Daten von Benzocyclanonen verglichen.

On étudie, par une méthode d'interaction de configurations, la série de conformères possibles de structure $C_6H_5C = O$. La dépendance sur l'angle dièdre C_6H_5—CO des énergies des états électroniques et des transitions, ainsi que les forces oscillatrices, est obtenue et comparée avec des données expérimentales pour les benzocyclénones. On examine finalement le rapport entre les propriétés physiques et l'angle dièdre et flexibilité du noyau cyclanique.

I. Introduction

In recent years many quantum-chemical calculations have been performed for complex organic molecules, with results often found reconcilable with experiment. Such an agreement alone does not ensure that the theoretical approach has taken account of all decisive factors; one has still to demonstrate that a given structural change in the molecule under study would produce a corresponding change, in the right direction, of the theoretical results. Thus calculations should be performed by the same model for a *series* of closely related compounds. The classical study of methyl-azulenes [1] or the recent investigation of several non-benzenoid aromatic compounds [2] illustrate this point.

Still, one feels that a "series of closely related compounds" is not simply a certain number of molecules, but a set of similar structures such that the difference between any two successive ones is small and simply expressible by means of a well-defined parameter, the inclusion of which does not introduce a novel subject of investigation. The results for the various structures in the set may then be considered as being of exactly the same validity, and the predicted *trend* of change in properties, rather than the numerical results for an isolated case, should serve in evaluating the reliability of the method.

Ideal cases for study are series of successive conformers obtained when two parts of a molecule, containing π-unsaturation, rotate about some internal single bond. The theoretical representation of the rotation necessitates merely the specification of some dihedral angle α. Experimentally, the effect may be followed by using molecules which contain, in addition to the system under study, another chemical group, of known steric effect and of minor electronic interaction. If agreement between experiment and theory (up to a calibrative factor) is not obtained, the influence of additional factors should then be investigated.

The problem may be illustrated by reference to the recently discussed question of stilbene geometry [3]. In order to find rotational angles in a stilbene derivative, e.g. *cis*-2-chlorostilbene, transitionenergies are calculated for several possible angles, then compared with experiment, and the most probable structure inferred. A critical test would now demand to study several derivatives of the compound, such that one be planar, the others not, and to examine whether the method predicts correctly the changes attending rotation.

We have recently described [4] a configuration interaction study of the phenylketone chromophore (Fig. 1); the present paper reports the results of calculations for the series of successive structures obtained upon rotation of the carbonyl about the *a*-*g* bond. As the rotation proceeds, the system passes from a coplanar state ($\alpha = 0°$; $a, b, \ldots g, h$ coplanar), through a region denoted as "aplanar" ($0° < \alpha < 90°$), to a final "perpendicular" situation ($\alpha = 90°$; plane $\{a, g, h\}$ perpendicular to $\{a, b, \ldots f\}$).

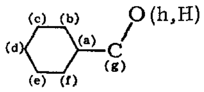

Fig. 1

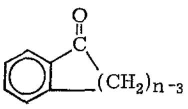

Fig. 2

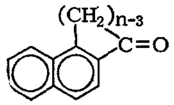

Fig. 3

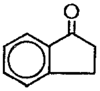

Fig. 4

Results are compared with published experimental values for the benzocyclenones (Fig. 2), hereafter referred to by the number n of atoms in their cyclenone moiety, so that n_5 indicates indanone (Fig. 3), etc. Of these, n_5 should be almost coplanar, and a study of molecular models suggests for n_6 the maximally-puckered half-chair conformation [5] with $\alpha \sim 30°$ (see, however [6, 7] for other analyses). Models alone do not suffice to establish the conformation when $n > 6$: the flexibility of the ring (which rises with its size) makes impossible any *a priori* prediction of the most probable geometry.

Some spectral data, compiled from various sources, are presented in Table 1. In the near UV spectrum, we observe the $n \rightarrow \pi^*$ transition, above 300 mμ, and two aromatic $\pi \rightarrow \pi^*$ bands, at about 280 and 240 mμ. Another band, at about 200 mμ, has apparently not been studied in this series, but is recorded [8] for the naphthocyclenones (Fig. 4). Comparing the planar n_5 with its higher homologs we note that, on the whole, all absorption bands shift bathochromically, and that absorptivity increases for the $n \rightarrow \pi^*$ transition and decreases for the other bands.

Table 1. *Experimental Data*

Compound	210 mμ abs. of naphthocyclenones	240 mμ $\pi \to \pi^*$ abs.					280 mμ $\pi \to \pi^*$ abs.			$n \to \pi^*$ transition	
		in non-polar solvent			in EtOH						
	$\lg\varepsilon^b$	λ	$\lg\varepsilon$	f	λ	$\lg\varepsilon$	λ	$\lg\varepsilon$	f	λ	$\lg\varepsilon^b$
n_5	~4.08^a	239^c	4.10	0.208	244^g	4.08	284^c	3.42	0.031	311	(1.4)
		244^c	4.02				292^c	3.41		324	(1.4)
										333	(1.4)
										347	(1.0)
										362	(0.4)^f
n_6	~4.25^a	243^c	4.06	0.196	247^g	4.05	286^c	3.19	0.024	325	(1.8)
		(247.5)^d	(4.06)				296^c	3.15		341	(1.7)
										354	(1.6)
										371	(1.1)^f
n_7	~4.38^a	240^c	3.95	0.153	246^g	3.97	281^c	3.08	0.019		
n_8		244^c	3.81	0.114	248^g	3.76	286^c	3.04	0.016		
n_9					245^e	3.69	~275^e				

[a] Ref. [8]; spectrum in EtOH.
[b] Estimated from curve.
[c] Ref. [7]; spectrum in heptane.
[d] Ref. [10]; spectrum in hexane.
[e] Ref. [6]; spectrum in EtOH.
[f] Ref. [11]; spectrum in cyclohexane.
[g] Ref. [9].

Introduction of the rotational angle into calculations implies the evaluation of molecular integrals for pairs of non-parallel orbitals [4]. One published scheme [12] achieves this for bielectronic integrals by correcting the Mataga-Nishimoto formula [13] for parallel orbitals in such a way that the ratio of the corrected expression to its original form equals the corresponding charged-sphere ratio; another approach

[14] uses directly this latter model. We preferred an analytical approach [15] based upon Slater orbitals. Monoelectronic bicentric integrals may be adjusted in the non-parallel case [12] by multiplying their exponential expression by cos α. In the present study they are considered proportional to overlap integrals, and these are calculated analytically.

In what follows, Section II outlines the method and Section III relates the results. Conclusion, with special reference to the benzocyclenone problem, is presented in Section IV.

II. Method

The method follows closely that already described [4, 15] and only an outline will be given here.

Nine atomic orbitals χ_i — the eight π-orbitals $a, b, \ldots h$ (Fig. 1) and the non-bonding oxygen orbital H — are used to construct eight molecular orbitals φ_i: the first five are the symmetry-determined benzene orbitals, the next two belong to the carbonyl moiety, and the last is the non-bonding χ_H. From these are constructed a ground configuration *GC* (energy taken as zero), with doubly occupied $\varphi_1, \varphi_2, \varphi_3, \varphi_7, \varphi_9$, and eight other configurations: benzene local excitations BL_1 ($\varphi_2 \rightarrow \varphi_4$), BL_2 ($\varphi_2 \rightarrow \varphi_5$), BL_3 ($\varphi_3 \rightarrow \varphi_4$), BL_4 ($\varphi_3 \rightarrow \varphi_5$), carbonyl local excitation CL ($\varphi_7 \rightarrow \varphi_8$), "charge-transfer" states CT_1 ($\varphi_2 \rightarrow \varphi_8$), CT_2 ($\varphi_3 \rightarrow \varphi_8$), and the *NE* configuration resulting upon $n \rightarrow \pi^*$ excitation ($\varphi_9 \rightarrow \varphi_8$). These configurations are used to construct a *CI* matrix.

The main difficulty lies in the choice of bond-lengths and bond-angles; in principal, each conformer should have its own set of such values (which can sometimes [16] be deduced theoretically). In view of the geometrical complexity of the system it was decided to use a fixed set of values for all conformers. All trigonal angles were taken as 120°, the benzene bond-length 1.397 Å [7], the distances φ-CO and C=O as 1.460 and 1.215 Å, respectively (based upon data [18] for 2-butenal, propynal and propenal).

The complete calculation was now repeated for eighteen successive conformations, beginning with the almost planar $\alpha = 5°$ and proceeding, by steps of 5°, to the perpendicular $\alpha = 90°$. At each rotational angle, each pair χ_p, χ_q of atomic orbitals ($p, q = a, b, \ldots h$, H) was written as

$$\chi_p = \alpha_p \chi_p^x + \beta_p \chi_p^y + \gamma_p \chi_p^z\,; \qquad \chi_q = \alpha_q \chi_q^x + \beta_q \chi_q^y + \gamma_q \chi_q^z$$

so that the expression of the Coulomb repulsion integrals [19] takes the form

$$\begin{aligned}(\chi_p \chi_p, \chi_q \chi_q) = {} & (3S_a, 3S_b)\,(P_1 + P_2 + P_3 + P_4) \\ & + (3/2)\,(3S_a, 3D \textstyle\sum_b)\,(2P_1 - P_2 - P_3 - P_4) \\ & + (3/2)\,(3D \textstyle\sum_a, 3S_b)\,(2P_1 - P_2 - P_3 + 2P_4) \\ & + (9/4)\,(3D \textstyle\sum_a, 3D \textstyle\sum_b)\,(4P_1 + P_2 + P_3 - 2P_4) \\ & + (27/4)\,P_6(3D\,\Pi_a, 3D\,\Pi_b) \\ & + (27/4)\,(3D\,\Delta_a, 3D\,\Delta_b)\,(P_2 - P_3 + P_5)\end{aligned}$$

where the factors P are

$$\begin{aligned} P_1 &= \gamma_p^2 \gamma_q^2\,, & P_2 &= \alpha_p^2 \alpha_q^2 + \beta_p^2 \beta_q^2\,, \\ P_3 &= \alpha_p^2 \beta_q^2 + \beta_p^2 \alpha_q^2\,, & P_4 &= \alpha_p^2 \gamma_q^2 + \beta_p^2 \gamma_q^2 + \gamma_p^2 \alpha_q^2 + \gamma_p^2 \beta_q^2\,, \\ P_5 &= 4\,\alpha_p \beta_p \alpha_q \beta_q\,, & P_6 &= 4\,\gamma_p \gamma_q (\alpha_p \alpha_q + \beta_p \beta_q)\,. \end{aligned}$$

Overlap integrals are expressed [19] as a combination of $S(2p\pi, 2p\pi)$ and $S(2p\sigma, 2p\sigma)$

$$S = (\alpha_p \alpha_q + \beta_p \beta_q)\, S(2p\pi, 2p\pi) + \gamma_p \gamma_q\, S(2p\sigma, 2p\sigma)\,.$$

In our scheme, these relations suffice to calculate all quantities occurring in *CI* matrix elements for whatever rotational angles. Matrix elements once found, the *CI* matrices are diagonalised to yield state-functions θ_i and state-energies E_i. These are used to calculate transitionmoments and oscillator strengths.

III. Results and Discussion

The Ground State, θ_0. Naturally, the main contributor to θ_0 is the ground configuration *GC*, yet a small *CT* contribution, diminishing with angle, is discernible. As a result, ground state energy is lower than the value corresponding to the non-interacting *GC*, with a lowering of 0.405 eV at 5° and 0.025 eV at 90°.

The First Electronic Transition, $\theta_0 \rightarrow \theta_1$. The next state, θ_1 in our notation, consists mainly ($>$ 99% at 5°, 92% at 90°) of the *NE* configuration, which represents the passage of non-bonding oxygen electron to the excited carbonyl π-orbital. Its energy (in respect to the energy of *GC*, taken as zero for each conformer separately), diminishes with rotation. As the rotational angle is raised, the energies of θ_0 and θ_1 approach each other, so that the $n \rightarrow \pi^*$ transition ($\theta_0 \rightarrow \theta_1$) is expected to shift bathochromically: calculated transition energies are 4.29 eV (= 289 mμ) at 5°, 3.64 eV (= 340 mμ) at 90°. The transition is found to be forbidden at both rotational extremes, but permitted to a certain extent in intermediate angles, having a calculated maximal oscillator strength of $f = 2.10^{-4}$ at 35°. These relations are depicted in Fig. 5.

It is difficult to verify these trends, owing to the rarity of published experimental data, but we may compare the results with values calculated [20] from the absorption curves [11] of planar indanone (n_5) and aplanar tetralone (n_6) (Table 1). The evolution of both transitionenergy and f seem to be borne out by experiment.

This result may be compared with overlap relationships in the series under study. As recently stated [21], the oscillator strength for the $n \rightarrow \pi^*$ transition in phenyl-ketones may be dependent either on the overlap between the aromatic orbitals and the carbon orbital g ([22], Fig. 1), or upon their overlap with the

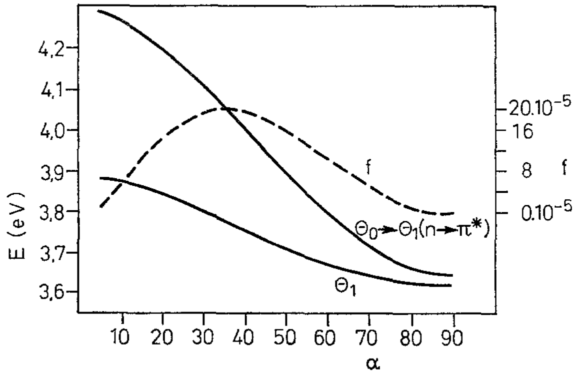

Fig. 5. First electronic transition

Table 2. "*BL*" *States at 5°*

$E_2 = \mathit{4.453},\ \Delta E = 4.858\ (\equiv 254\ \mathrm{m\mu}),\ f_{02} = 0.030$
$\theta_2 = -0.103\, GC + 0.218\, CT_1 + 0.016\, CT_2 + \mathit{0.719}\, BL_1$
$-0.008\, BL_2 + 0.018\, BL_3 - \mathit{0.644}\, BL_4 - 0.084\, CL - 0.034\, NE$

$E_3 = \mathit{5.218},\ \Delta E = 5.623\ (\equiv 221\ \mathrm{m\mu}),\ f_{03} = 0.585$
$\theta_3 = -0.035\, GC + 0.023\, CT_1 + 0.352\, CT_2 - 0.011\, BL_1$
$-\mathit{0.392}\, BL_2 + \mathit{0.843}\, BL_3 + 0.050\, BL_4 - 0.078\, CL + 0.003\, NE$

$E_4 = \mathit{6.055},\ \Delta E = 6.461\ (\equiv 192\ \mathrm{m\mu}),\ f_{04} = 0.220$
$\theta_4 = 0.009\, GC + 0.007\, CT_1 + 0.234\, CT_2 + 0.029\, BL_1$
$+\mathit{0.913}\, BL_2 + \mathit{0.328}\, BL_3 + 0.033\, BL_4 + 0.031\, CL + 0.001\, NE$

$E_5 = \mathit{6.359},\ \Delta E = 6.764\ (\equiv 183\ \mathrm{m\mu}),\ f_{05} = 0.625$
$\theta_5 = -0.188\, GC + 0.612\, CT_1 - 0.026\, CT_2 + \mathit{0.293}\, BL_1$
$+0.010\, BL_2 - 0.074\, BL_3 + \mathit{0.610}\, BL_4 - 0.352\, CL - 0.022\, NE$

oxygen non-bonding orbital H [23]. In our calculations we find that the overlap integral between orbital a and any of the carbonyl orbitals, as well as S_{bg}, change monotonously with angle. On the other hand, overlap $S_{b\mathrm{H}}$ has a maximum at 35 – 40° (and overlap $S_{b\mathrm{H}}$ — at 40 – 45°), in line with the second of the possibilities mentioned above.

Another property which has an extremum at 35° is the change in the contribution of *CT* configurations upon $n \to \pi^*$ excitation. As the rotational angle is raised, the *CT* contribution to θ_0 diminishes from 4.97% at 5°, 3.5% at 35° to 0% at 90°; concurrently, *CT* contribution to θ_1 augments through 0.09%, 3.35% and 7.62% at these respective angles. Thus, the $n \to \pi^*$ transition is accompanied by diminishing *CT* for $\alpha < 35°$, by increasing *CT* for $\alpha > 35°$.

Benzene Local Excitations. The next four *CI* wave-functions, together with their energies, transitionenergies from θ_0 and oscillator strengths, are given in Table 2 for the almost planar conformation of 5°. They consist mainly of *BL* configurations (93%, 86%, 94%, 46%) and are characterizable as excited states of the benzene moiety, so that they might be studied in the frame of D_{6h} properties. The configurations BL_2 and BL_3, which transform according to the same representation of the D_{6h} group, are combined to yield two functions: $(1/\sqrt{2})\,(BL_2 + BL_3) \in B_{1u}$ and $(1/\sqrt{2})\,(-BL_2 + BL_3) \in B_{2u}$. Also, two linear combinations transforming according to the E_{1u} representation, $(1/\sqrt{2})\,(BL_1 + BL_4)$ and $(1/\sqrt{2})\,(BL_1 - BL_4)$ are formed from the degenerate pair BL_1, BL_4.

When account is being taken of the carbonyl group (that is, the present case) but a *CI* treatment *not* carried out, *three BL* states are found: BL_1 and BL_4 are degenerate (5.829 eV, independent of angle), with energy contained between that of BL_2 (5.925 at 5°, 5.880 at 90°) and of BL_3 (5.732 at 5°, 5.797 at 90°). Introducing configurational interaction, these levels disperse over a wider energy region, forming the wave-functions θ_2, θ_3, θ_4, θ_5. The low-energy θ_2, related to E_{1u} symmetry, contains small contributions of *CT*, *CL* and *NE* configurations; the high-energy θ_5 contains considerable contributions of CT_1 and *CL*. The intermediate θ_3 and θ_4, related to B_{2u} and B_{1u}, are formed from interacting BL_2 and BL_3. The transitions $\theta_0 \to \theta_2$, $\theta_0 \to \theta_3$, $\theta_0 \to \theta_4$ and $\theta_0 \to \theta_5$ are, respectively, weak,

Table 3. "*BL*" *States at 90°*

$E_2 = 4.591, \Delta E = 4.616$ (≡ 269 mμ), $f_{02} = 0.051$
$\theta_2 = -0.003\, GC + 0.007\, CT_2 + 0.707\, BL_1 - 0.706\, BL_4 - 0.006\, CL$

$E_3 = 5.509, \Delta E = 5.534$ (≡ 224 mμ), $f_{03} = 0.870$
$\theta_3 = 0.009\, CT_1 - 0.661\, BL_2 + 0.750\, BL_3 - 0.005\, NE$

$E_4 = 6.167, \Delta E = 6.193$ (≡ 201 mμ), $f_{04} = 0.062$
$\theta_4 = -0.017\, CT_1 + 0.750\, BL_2 + 0.661\, BL_3 + 0.007\, NE$

$E_5 = 7.007, \Delta E = 7.033$ (≡ 178 mμ), $f_{05} = 1.361$
$\theta_5 = -0.035\, GC - 0.038\, CT_2 + 0.689\, BL_1 + 0.691\, BL_4 - 0.210\, CL$

strong, fairly strong and very strong. The predicted changes which occur upon rotation are typified by comparing Table 2 with Table 3.

Experimentally, three absorption regions have been observed in the *BL* region of the phenyl-ketone UV spectrum (Table 1): the weak ($f \sim 0.020$) "benzene ring absorption" [7] occurs around 280 mμ, a strong one ($f \sim 0.114 - 0.224$) around 240 mμ, and a third transition (unstudied) at about 200 mμ. Tentatively, we may identify these three with $\theta_0 \rightarrow \theta_2$, $\theta_0 \rightarrow \theta_3$ and $\theta_0 \rightarrow \theta_4$, θ_5. The direction of polarization corroborates the assignments [24]. We denote by X the long axis *d-a-g* (Fig. 1), by Y — an axis contained in the $a, b, \ldots f$ plane and perpendicular to X, and by Z — the third cartesian axis. Then, $\theta_0 \rightarrow \theta_2$ is polarized in the $a, b, \ldots f$ plane almost along Y,

$$|X| = 0.340, \quad |Y| = 1.036, \quad |Z| = 0.003 \text{ at } 5°,$$

and

$$|X| = 0.405, \quad |Y| = 1.277, \quad |Z| = 0. \quad \text{at } 90°.$$

The transition $\theta_0 \rightarrow \theta_3$ is almost polarized along the X-axis as the phenyl and carbonyl become perpendicular

$$|X| = 0.378, \quad |Y| = 0.496, \quad |Z| = 0.002 \text{ at } 5°,$$

and

$$|X| = 0.331, \quad |Y| = 0.073, \quad |Z| = 0. \quad \text{at } 90°.$$

The calculations show that both $\theta_0 \rightarrow \theta_3$ and $\theta_0 \rightarrow \theta_4$ transitions shift bathochromically as the rotational angle increases. This prediction agrees with the experimentally known trend. The angle-dependence of θ_3-energy and $\theta_0 \rightarrow \theta_3$ transition-energy is depicted in Fig. 6.

On the other hand, the calculated f-values (shown in Fig. 6 for the transition $\theta_0 \rightarrow \theta_3$) increase with α, whereas experimentally they are known to decrease. A possible explanation is that transition moments were evaluated from purely electronic wave-functions, account not being taken of the difference in population between the vibronic sub-levels of the ground and excited states. What one actually observes [25] is not the 0–0 transition, but a vibronic transition corresponding to a torsional vibration along the *a-g* bond. The diminution of the oscillator strength, observed experimentally as one passes from indanone (n_5) to its higher homologs, as well as the high f-value found for the non-rigid acetophenone ($f = 0.224$ [7]), seem to indicate that the geometry of the excited state is different

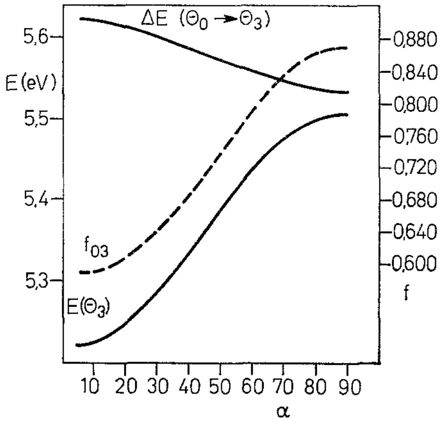

Fig. 6. Third electronic transition

from that of the ground state and that this difference augments with *n*. A similar argument has been offered [26], although criticized [27], in the literature.

In addition to this, we remember that the same bond-lengths and bond-angles have been used throughout the series, while it is clear that their actual values influence the properties of the transition. This has been shown, for example, in the cyclanone series [28].

The two transitions $\theta_0 \to \theta_4$ and $\theta_0 \to \theta_5$ (Tables 2 and 3) are of similar energy at 5°, but get removed from one another as the rotation proceeds: the difference in energy is 0.30 eV at 5°, 0.46 at 45° and 0.84 eV at 90°.

Charge Transfer States. By construction, there are two charge-transfer states, θ_6 and θ_7, of similar energy. Some numerical values are given in Table 4.

An interesting point, related to the symmetry of the phenyl-ketone structure, is best brought out in connection with the *CT* states. The only symmetry element (beside the identity) of the completely planar conformation is a reflection across the molecular plane in relation to which all atomic orbitals, except χ_H, and all molecular orbitals, except φ_9, are antisymmetric, and all configurations, except *NE*, are symmetric. There are obtained one pure *NE*, and eight other mixed states (subject to restrictions by benzene local symmetry). On the other rotational extreme, however, the symmetry plane is perpendicular to the benzene ring, passing through atoms *a*, *d*, *g*, *h*. In this case, φ_1, φ_2, φ_4, and φ_9 are symmetric, while φ_3, φ_5, φ_7, and φ_8 are antisymmetric, and we obtain five interacting symmetric configurations (GC, CT_2, BL_1, BL_4, CL) and four interacting antisymmetric ones

Table 4. *Energies of "CT" States*

Angle	5°	45°	90°
E_6	7.550	7.401	7.143
$\Delta E\ (\theta_0 \to \theta_6)$	7.955	7.618	7.168
E_7	7.654	7.537	7.227
$\Delta E\ (\theta_0 \to \theta_7)$	8.060	7.754	7.253

Table 5. *Wave Functions (Except "BL") for 90°*

n	E_n	θ_n
0	−0.025	$0.998\,GC - 0.004\,CT_2 + 0.020\,BL_1 + 0.015\,BL_4 - 0.050\,CL$
1	3.620	$0.276\,CT_1 - 0.003\,BL_2 + 0.961\,NE$
6	7.143	$0.960\,CT_1 + 0.021\,BL_2 + 0.005\,BL_3 - 0.276\,NE$
7	7.227	$0.002\,GC + 0.998\,CT_2 + 0.015\,BL_1 + 0.026\,BL_4 - 0.044\,CL$
8	8.404	$0.044\,GC + 0.036\,CT_2 + 0.155\,BL_1 + 0.140\,BL_4 + 0.975\,CL$

(CT_1, BL_2, BL_3, NE). Four of the states obtained from these were given in Table 3; the remaining are presented in Table 5.

The conformational change is thus accompanied by passage from one symmetry-state to another, and some of the configurations that mix at 0° cannot interact at 90°. Calculations show that the change occurs about one of the singular angles 30° or 60°. To illustrate this, we denote the coefficient of CT_1 in θ_6 by C_{61}, of CT_2 in θ_6 by C_{62}, and likewise C_{71} and C_{72}. At 0°, CT_1 and CT_2 mix freely, so that C_{61} and C_{62}, as well as C_{71} and C_{72}, are of about equal value; these values change gradually up to 60°. In the region about 60°, all coefficients have extremum values, and a rapid change toward their values at the final symmetry state is discerned. At 90°, CT_1 and CT_2 do not interact, and we find $C_{62} = C_{71} = 0$, $C_{61} \sim 1$, $C_{72} \sim 1$. This analysis is representative as long as the *absolute* coefficient values are considered; if account is also taken of signs (Fig. 7) another singular region, 70° — 75°, is revealed.

Interaction matrix elements behave therefore in such a way, that CT states are, up to about 75°, in their initial symmetry, and from 75° on — in their final symmetry.

IV. A Note on Benzocyclenones

Probably, the most significant point about the data in Table 1 is that one cannot order the molecules consistently according to the evolution of their various spectral properties. Thus, the bathochromic shift of the 240 mμ band (considered [7, 9] to be the most revealing property) increases in the order n_5, n_9, n_7, n_6, n_8, while the corresponding order for the 280 mμ band is n_9, n_7, n_5, n_6 — n_8. In both

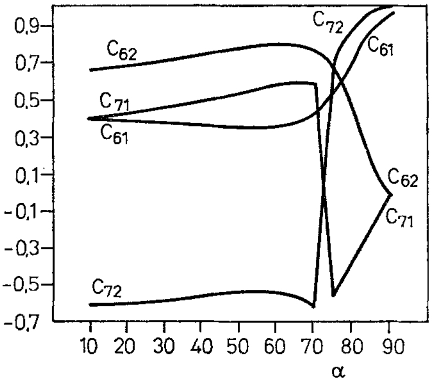

Fig. 7. Configuration Mixing in CT-states

bands, the molar extinction decreases as cyclenone ring-size increases (n_5, n_6, n_7, n_8, n_9). Therefore, some of these properties are not monotonous functions of the rotational angle. Now, all calculated values, except f_{01}, either increase or decrease with angle, and we infer that a certain factor, which affects the trend of change, is missing in the scheme. We note that to arrive at this conclusion, the complete study reported above was necessary, because every *single* calculation could have been "reconciled" with experiment.

Considering the 240 mμ absorption, we note that twisting a planar structure ($n = 5$) to an aplanar ($n \neq 5$) conformation, is accompanied by wave-length increase and extinction decrease. As the first of these phenomena is accounted for by our calculations, we may attempt a prediction of the rotational angles. Calibrating the results with $\alpha = 5°$ for n_5 and $\alpha = 30°$ for n_6 (the Dreiding model angle for the maximally-puckered half-chair form), we get $\alpha = 25°$ for n_7, $\alpha = 35 - 40°$ for n_8, $\alpha = 15°$ for n_9. Now, if the disagreement between observed and calculated oscillator strengths is really related to hindered vibrational levels, we may introduce the relation 2.817 ($f_{\mathrm{obs}}/f_{\mathrm{calc}}$) as a measure of ring rigidity. Applying this index to the various compounds, we find 1.00 for n_5 (most rigid), 0.86 for n_6, 0.69 for n_7 and 0.48 for n_8 (least rigid).

Investigation of molecular models shows that the dihedral angles suggested above constitute a compromise between the tendency to achieve a resonance-stabilized planarity and the tendency to alleviate non-bonding interactions by puckering. We conclude that transition energies are a measure of the rotational angles, whereas observed extinction coefficients may be related to ring-size.

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