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Rotatory Strength Calculations of Chiral Conformations of Acetone

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Summary The rotatory strength, R, of chiral conformers of acetone is proportional (but opposite in sign) to $\theta(n) - \theta(\pi^*)$; $\theta(n)$ and $\theta(\pi^*)$ represent twists of the n and π^* orbitals of the oxygen atom of the carbonyl group.

Our analysis of the c.d. data on amino ketones[1] and the work on the effect of substituents on the rotational strength of the chiral ketones[2] had indicated that the ground state played a more important part than the excited state in determining chirality. In order to test this hypothesis and to provide, if possible, a theoretical basis, we have calculated the rotatory strengths of chiral conformers of acetone as a model (Figure 1), using single determinant CNDO/2 including two-centre terms of electric and magnetic transition moments.[3] The results are presented in Figure 2: several conclusions can be deduced from them, of which decidedly the most important is our finding 4, that for this system, at least, both the sign and magnitude of rotatory strength can be predicted from ground-state wave functions. Subsequent calculations on β-amino ketones[4] and fluoro ketones,[5] whose results are in good agreement with experimental data, show that this concept is generally valid; thus, the immediate value of the present calculations (which are, however, still quite closely related to experimental data), is transcended by the generalisations that can be derived from them.

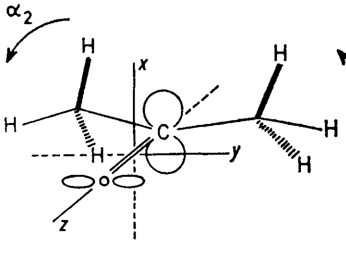

FIGURE 1. α_1 and α_2 are anticlockwise as observed along the C–C bond from the carbonyl carbon.

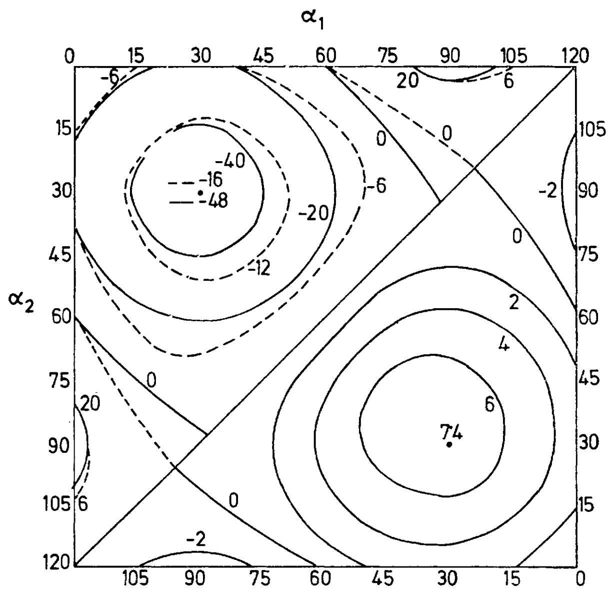

FIGURE 2. The twists $\theta(n)$ (– – –), $\theta(\pi^*)$ (———) and rotatory strength R (———) of acetone conformers.

Our conclusions in detail on the present model are as follows:

1. The carbonyl chromophore includes all bonds on both α carbons that overlap with π/π^* orbitals.
2. The individual contributions of the α and α′ 'axial' bonds to the rotatory strength, R, are not additive.
3. The rotatory strength $R(n_0 \rightarrow \pi^*)$ of an α axially oriented C–H bond is of the same sign as that of α axially oriented alkyl groups in the same octant but much smaller in magnitude.
4. The sign of the rotational strength $R(n_0 \rightarrow \pi^*)$ is opposite to that of $\theta(n_0)$ and $\Delta\theta = \theta(n_0) - \theta(\pi^*)$. For an $n \rightarrow \pi^*$ transition with both orbitals strictly localised on the C=O chromophore one finds from relationship (1):

$$R_{ij} = -\frac{C}{\Delta E}<\psi_i|\nabla|\psi_j>\cdot<\psi_j|r\times\nabla|\psi_i> \qquad (1)$$

(a) that the magnetic transition moment is virtually constant and (b) that $R = ca. -\Delta\theta$ (due to the variation of the electric moment†). If both orbitals are, more realistically, partly delocalised, R_{ij} will depend, in the first approximation, linearly on both $\theta(n_0)$ and $\theta(\pi^*$: $R(n_0 \rightarrow \pi^*) = C(n_0)\theta(n_0) + C(\pi^*)\theta(\pi^*)$ where $C(n_0) = -C(\pi^*)$ no longer holds. Subjecting the data in Figure 2 to a least square analysis yields $C(n_0) = -0{\cdot}56$, $C(\pi^*) = 0{\cdot}04$, indicating that R depends almost entirely on ground-state effects. The precise values of $C(n_0)$ and $C(\pi^*)$ will change from system to system but the general conclusion is borne out by our studies on larger molecules, where $\theta(n_0)$ attains considerably higher values.[4,5]

The same treatment of the $\pi \rightarrow \pi^*$ transition yields $C'(\pi) = 0{\cdot}75$, $C'(\pi^*) = -0{\cdot}14$; therefore the rotatory strength of this transition is also governed by the ground state wave function.[4,5,6]

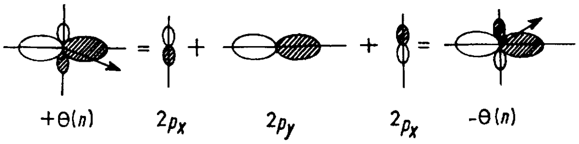

FIGURE 3. Mixing of $2p_y$ and $2p_x$ oxygen orbitals; θ_{n_0} and θ_{π^*} are defined as:

$$\tan\theta_{n_0} = C^{n}{}_{p_x}/C^{n}{}_{p_y}$$

$$\tan\theta_{\pi^*} = -C^{\pi^*}{}_{p_y}/C^{\pi^*}{}_{p_x}.$$

Throughout the rest of this and the accompanying communications, the subscripts and superscripts have been placed in parentheses for convenience.

In terms of one of the previous theoretical analysis of the foundations of the Octant Rule[7] our interpretation, in fact, comes down to the mixing in of π and/or π^*, rather than of $3d$ orbitals on the C=O group, in that the lone pair shows a small π_x component which is responsible for chirality (Figure 3). In principle, it is thus possible to predict consignate (octant) or dissignate (antioctant) behaviour by employing even semi-empirical MO calculations (*e.g.* CNDO/2 with all its shortcomings gives quite realistic results[3] and does predict chiral behaviour of fluorine substituents).[5] The problem is reduced to one of predicting orbital shapes.

The above conclusions support some empirically derived rules for the rationalisation of c.d. data, such as the axial bond chirality concept for αβ-unsaturated ketones,[8,9] conjugated dienes,[10] and α-diketones.[11]

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† This is borne out by experimental data establishing a linear relationship, $R = ca. \sqrt{D}$; G. Snatzke and G. Eckhart, *Tetrahedron*, 1968, **24**, 4543.

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