Journal of

The Chemical Society,

Chemical Communications

NUMBER 17/1976 1 SEPTEMBER

Analysis of the Unusually Large Rotatory Strength of (+)-(1*S*,5*S*)-Bicyclo[3.2.0]heptan-3-one

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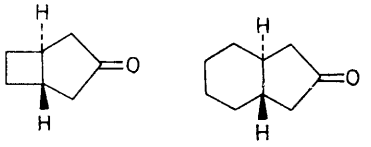
Summary The unusually large rotatory strength recently reported for the $n \rightarrow \pi^*$ transition of (+)-(1*S*,5*S*)-bicyclo-[3.2.0]heptan-3-one is found to arise primarily from the twist of the cyclopentanone unit, as shown by a CNDO/S molecular orbital model.

Recently Windhorst[1] has reported the synthesis and chiroptical properties of (+)-(1*S*,5*S*)-bicyclo[3.2.0]heptan-3-one (I), noting the unusually large rotatory strength, for a saturated ketone, of the 300 nm ($n \rightarrow \pi^*$) transition. He obtained a value of the rotatory strength R of $+21{\cdot}3$ $(100/D\beta)$‡ in iso-octane. This value is several times



(I) (II)

larger than normal for a saturated ketone, and is only a factor of 3 smaller than that exhibited by Weissberger's compound,[2] in which many atoms fall within octants associated with positive contributions to the c.d.[3] It is of interest, therefore, to examine more closely the origins of the intense c.d. band in (I).

We have recently shown[4] that reliable comparisons of the rotatory strengths of the $n \rightarrow \pi^*$ transition in saturated ketones are obtained using the CNDO/S method of Del-Bene and Jaffé,[5] but without the use of configuration interaction. Experimental data for a large number of ketones were successfully correlated in this model, and a non-symmetry-determined third nodal surface was constructed, separating 'front' and 'back' octants.[4]

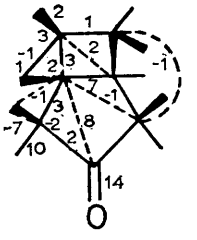


Figure 1. Contributions to $\langle n|\nabla_z|\pi^*\rangle$, in atomic units $\times 10^{-3}$, for (I). Terms not shown can be inferred from the C_s symmetry, or are < 1 in the units used. Nonbonded interactions are indicated by dashed lines.

Calculations have been carried out in this model for (I), and for (+)-(1*S*,6*S*)-bicyclo[4.3.0]nonan-8-one, (II); cyclopentanone, twisted as in (I) and (II), was also examined in order to evaluate the contribution of the ring twist itself. Geometries for these compounds were obtained by inspec-

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‡ R(S.I.) $= 1{\cdot}03 \times 10^{-63} R(100/D\beta)$. There is an apparent error in the exponents of R(S.I.) as quoted by Windhorst (ref. 1).

tion of molecular models, with all C–C bonds *ca.* 1·54 Å, C–H 1·08 Å, and C–O 1·22 Å. The twist angle in the cyclopentanone unit is estimated to be *ca.* 35° in (I), and *ca.* 27° in (II).

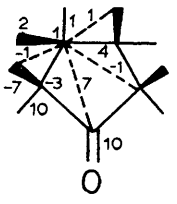

FIGURE 2. Contributions to $<n|\nabla_z|\pi^*>$, as in Figure 1, for the cyclopentanone unit of (I).

The results are: compound (I): λ_{max}(calc.) 279 nm, R(calc.) +90·3, R(expt.)[1] +21·2; cyclopentanone unit: λ_{max}(calc.) 312 nm, R(calc.) +67·4; compound (II): λ_{max}(calc.) 294 nm, R(calc.) +27·1, R(expt.)[1] +16·5; cyclopentanone unit: λ_{max}(calc.) 328, R(calc.) +4·5. All R values are in reduced units ($100/D\beta$), and are calculated using the dipole velocity form of the electric dipole transition moment. We place no special significance on the absolute magnitudes we calculate in this model, but instead concentrate here on the relative values. As expected, the magnitudes of the rotatory strengths are quite sensitive to the dihedral twist angle of the 5-membered ring.

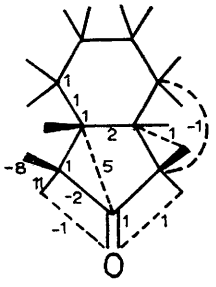

FIGURE 3. Contributions to $<n|\nabla_z|\pi^*>$, as in Figure 1, for (II).

The $n\rightarrow\pi^*$ transition is magnetic-dipole allowed, and electric-dipole forbidden in the isolated chromophore. The magnetic moment has a magnitude of *ca.* 1 Bohr magneton, directed along the C=O bond axis, for all the compounds listed. Thus, changes in the parallel (z) component of the electric dipole transition moment control the magnitude of the rotatory strength. This component is expressed as $<n|\nabla_z|\pi^*>$ in the dipole velocity form, and may be analysed into one- and two-centre contributions by summing over all the atomic orbital matrix elements involved, and multiplying by the appropriate molecular orbital coefficients. The results, shown in Figures 1—4, indicate that the twisting of the 5-membered ring is primarily responsible for the rotatory strength in (I), although it is enhanced by the twist of the 4-membered ring. Indeed, inspection of a model shows that the bridgehead carbon atoms are the only part of the carbon skeleton that is significantly out-of-plane. Our findings are thus consistent with the major conclusion of Richardson, *et al.*[6] Differences between the present analysis and theirs show up, however, in the calculations for (II) and its 5-membered ring fragment. Richardson, *et al.*[6] found that for a dihedral twist angle of 23·6°, the computed rotatory strength of cyclopentanone is *ca.* 25% larger than that estimated for 3*eq*,4*eq*-dimethylcyclopentanone, which is taken to mimic

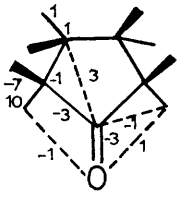

FIGURE 4. Contributions to $<n|\nabla_z|\pi^*>$, as in Figure 1, for the cyclopentanone unit of (II).

the hydrindanone system. The present results indicate, on the contrary, that the presence of the additional 6-membered ring should enhance the optical activity of the $n\rightarrow\pi^*$ transition by a factor of *ca.* 6. In the population analysis this is traceable to the difference in sign of the two-centre C–O contribution to $<n|\nabla_z|\pi^*>$ in the two cases. This difference in sign is a consequence of a sign change in the mixing of the $2p_x(\pi)$ atomic orbitals on the carbonyl group with the $2p_y$ orbitals taking part in the n orbital. The experimental values of $R = +9·9$ for (+)-3-methylcyclopentanone and $R = +16·1$ for (II) quoted by Richardson, *et al.*,[6] moreover, appear to correlate more closely with the present calculations than with theirs.

I thank Professor A. Moscowitz for calling the work of Windhorst to my attention. Support for this work is provided by the Danish N.A.T.O. Science Committee, and by the George C. Marshall Memorial Fund in Denmark.

(*Received, 24th June* 1976; *Com.* 712.)

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