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STERIC EFFECTS ON THE ULTRAVIOLET ABSORPTION OF THE AROMATIC RINGS IN 2,3-*endo*, *cis*-DIPHENYL-5-SUBSTITUTED BICYCLO [2.2.1] HEPTANE SYSTEMS

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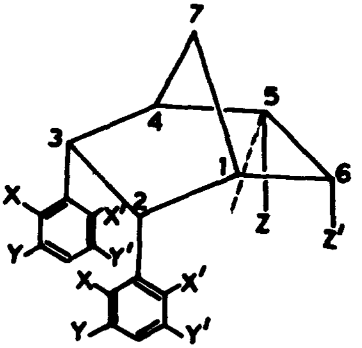
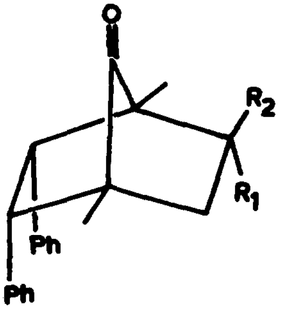
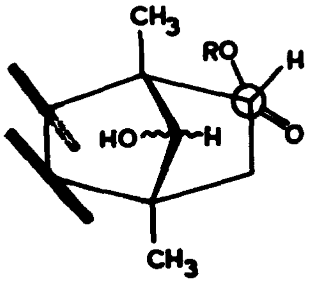
Midway through a study of the possibility of occurrence of atropisomerism of aryl rings in 2,3-*endo*, *cis*-diarylbicyclo [2.2.1] heptanes, substituted in the specific different ways indicated in I, we have found that an *endo*-substituent at C_5 (Z in I) can so constrain the rotomeric conformation of unsubstituted phenyl rings that steric-UV effects become manifest.



I: XX' (X ≠ X') exclude
YY' (Y ≠ Y') and
vice versa for given
ZZ' (Z either = or ≠ Z')

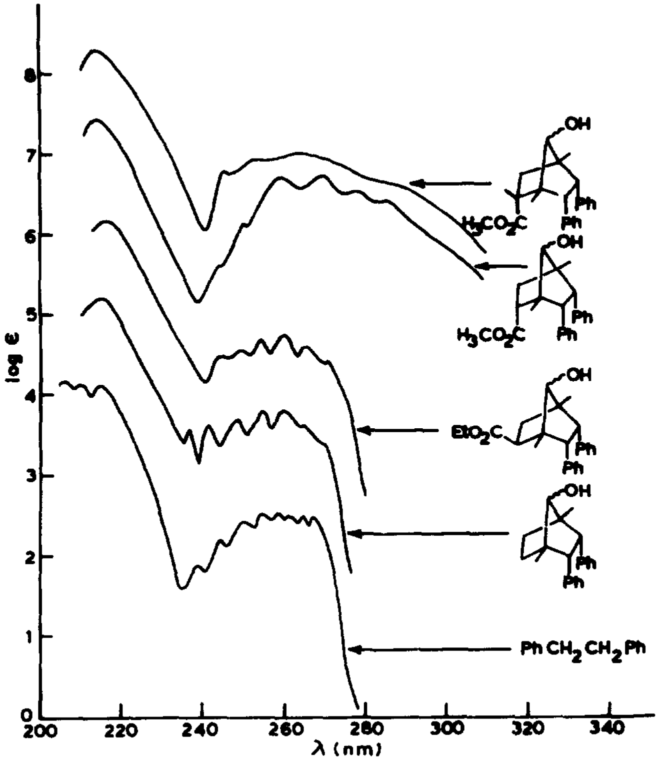


IV: $R_1 = R_2 = H$
V: $R_1 = CO_2Me; R_2 = H$
VI: $R_1 = CO_2Me; R_2 = Me$
VII: $R_1 = H ; R_2 = CO_2Me$



VIII

In their, now classic, work on paracyclophanes Cram et al.[1] sought to study the steric-UV effect of bringing two benzene rings close to each other, face to face, in isolation from effects caused by their warping (established for [2.2] paracyclophane[1]), by comparing the UV absorption characteristics of *cis*-1,2-diphenylcyclopentane (II) with those of its *trans*-analogue (III) or with those of 1,2-diphenylethane or α,ω-(*p*, *p*'-dialkyl) diphenylalkanes. However, the absorption envelopes of all these systems were closely similar[2], underlining the possibility that the π-systems in II are not subject to steric compression because the alicycle in this system preferentially adopts an unsymmetric puckered conformation in which the aralkyl bonds are not eclipsed. While the possibility that steric-UV effects may yet be observed in a system like II if the phenyl groups were held eclipsed by appropriate tight bridging (e.g. as in IV) remained untested^3, Curtin et al.^{4} found that the resonances due to the aromatic protons in II form a broad multiplet (in contrast with the narrow absorption found for III) the width of which decreased on raising the temperature, consistent with the interpretation that rotation of the phenyl groups was biased at ambient temperature.



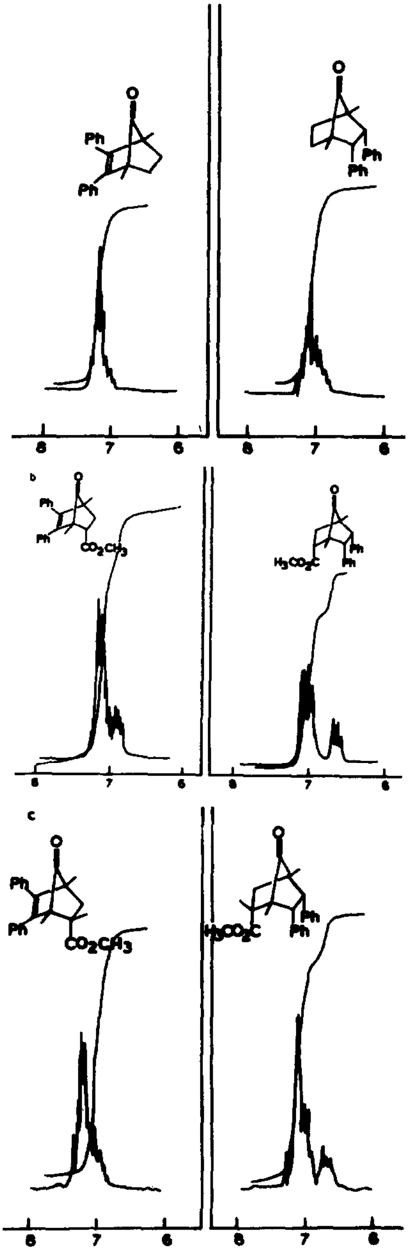


FIGURE 1; UV Spectra in EtOH of the indicated compounds. Curves succeeding the lowermost have been displaced upward by 1,2,3 & 4 log ε units.

FIGURE 2: The "aromatic regions" of the NMR spectra of the indicated compounds (in $CDCl_3$; δ units *ex* TMS). Curves a & c at 60 MHz and b at 100 MHz.

The stilbene precursors of IV, V and VI are, respectively, the products of $[4\pi + 2\pi]$ cycloaddition of cyclone to ethylene, methyl acrylate and methyl methacrylate; in the reactions leading to the esters the isomers with the ester groups endo-oriented are known to preponderate[5] and the stilbene precursors of V and VI were isolated by fractional crystalisation. The phenyl groups in IV were assigned endo (cis)-configuration by analogy with the cases of V & VI for which the —OMe resonances were found to be shifted upfield by ca 0.55 ppm on catalytic hydrogenation of their respective precursors[6].

As the carbonyl $n \rightarrow \pi^*$ absorption was found to interfere with any judgement as to whether systems IV→VI were exhibiting steric-UV effects these compounds were converted into the corresponding mixtures of syn and anti C_7-alcohols by reaction with borohydride[7]. As the reproduced UV spectra (Figure 1) of the reduced products indicate the C_5-unsubstituted case as well as the exo-ester VII show structured UV absorption which cuts off at about 280 nm, resembling "normal" cases (e.g. 1,2-diphenylethane). The endo-esters, however, exhibit relatively higher absorptivity beyond 300 nm. Interestingly, loss of fine structure is found for the α-methylated ester VI.

The aromatic regions of the ambient temperature NMR spectra of IV, V & VI and of their stilbene precursors are reproduced in Figure 2. While the spectra of IV and its precursor bear striking resemblance to the low and high temperature spectra of II[4], those of the esters V & VI separate into two sets of lines with the low and high field sets integrating approximately to 8 and 2 protons respectively, consistent with the notion that rotomeric orientations of the benzene rings, which place 2 protons of the ring at C_2 not only within the shielding region of that at C_3 but at 'inside' locations (structure VIII), are stabilized.

These observations collectively allow the interpretation that in systems like IV compression of π-systems to the degree that would engender large steric-UV effects is possible only when the phenyl groups are forced to adopt the rotomeric conformation schematized in VIII by a C_5-substituent. α-Methylation seems to open out the topside bonds of C_5 so that the C_5-ester bond becomes angled (dotted line I) in the manner that would bring the ester group nearer the C_2-phenyl whereby the more extreme rotomeric conformation forced on the latter compresses the π-systems further[8].

REFERENCES AND NOTES

1. D.J.Cram, N.L.Allinger and H.Steinberg, *J.Amer. Chem. Soc.*, **76**, 6132 (1954).

2. Reproducible differences are said to be found in the fine structure of the UV spectra of II and of its *trans*-analogue, III[4].

3. Stereomodels ("FMM", Prentice-Hall, Englewood Cliffs, N.J., U.S.A.) of IV indicated that, in the conformation of apparent, otherwise minimal, steric interaction, which has a plane of symmetry, the aralkyl bonds eclipse each other, with the interphenyl distance parameters, in a static situation, spanning the values for [3.3] paracyclophane (A, "abnormal" UV) and [4.4] paracyclophane (B, "normal" UV) [for IV phenyl C_1-$C_1' \approx 2.50$ Å and C_4-$C_4' \approx 4.10$ Å; for A[1]: C_1-C_1'=C_4-C_4'=2.52 Å and for B[1]: 3.73 Å]; these values were not too dissimilar to those of [3.4] paracyclophane [1][C_1-C_1'= 2.84 Å and C_4-C_4'= 3.41 Å] which is the first in the paracyclophane series to show abnormal UV and in which the axes perpendicular to the plane of the benzene rings are not collinear.

4. D.Y.Curtin, H.Gruen, Y.G.Hendrickson and H.E.Knipmeyer, *J.Amer Chem. Soc.*, **83**, 4838 (1961); *ibid*, **84**, 863 (1962).

5. K.N.Houk and L.J. Luskus, *J.Amer.Chem.Soc.*, **93**, 4606 (1971)

6. Allowing for "free" rotation of the CO_2 Me group at C_5, while preserving its internal conformation [R.L. Vold and R.R.Vold, *J.Magnetic Res.*, **13**, 38 (1974)], required the phenyl groups to assume the conformation schematized in VIII. At the conformation of apparent minimal interaction the locus of the ester methyl seemed to stay entirely within the shielding region of the proximate phenyl group as the ester group was rotated. The upfield shift was not found for the *exo*-ester, VII.

7. The change in the interphenyl distance parameters concomitant to the change in the coordination at C_7 was considered unlikely to affect the investigation seriously.

8. In the earlier version of this Letter the authors drew erroneous conclusions from inadequate experimental premises. They are deeply indebted to a referee for setting them on, what they now believe to be, the right track.