

The Molecular Structure of a Diels–Alder Adduct of an Azepine

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CURRENT theoretical¹ and experimental² interest in additions of dienophiles to cyclic polyenes prompts us to report a study of the reaction between tetracyanoethylene and *N*-ethoxycarbonylazepine (I) which is known to give a 1:1 adduct tentatively assigned the unprecedented structure (II) by Hafner.³ In our hands this adduct [55% yield, m.p. 156–157°, λ_{\max} (MeOH) 244 m μ , $\log \epsilon$ 3.88]⁴ exhibited an n.m.r. spectrum⁵ which was incompatible with either the symmetrical formula (II) or with the tricyclic alternative (III), but was

consistent with structure (IV). To obtain more definitive evidence the adduct was converted by bromine in methanol at 0° into a crystalline methoxybromide (70% yield, m.p. 191–192° dec.) which was subjected to single-crystal *X*-ray structure analysis.

The crystals were found to be monoclinic with symmetry $P2_1/n$ and $a = 13.50$, $b = 11.55$, $c = 10.79$ Å, $\beta = 94.46^\circ$, and $Z = 4$. The structure was solved using the heavy-atom method *via* conventional Patterson and Fourier techniques,

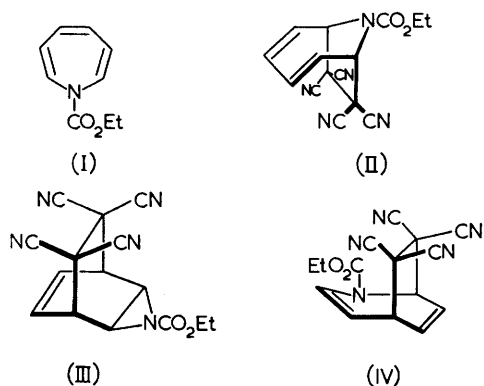
¹ R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

² E. Vogel, R. Schubart, and W. Böll, *Angew. Chem.*, 1964, **76**, 535; E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, 1965, 609.

³ K. Hafner, *Angew. Chem.*, 1963, **75**, 1041.

⁴ Satisfactory C, H, N analyses were obtained for all compounds characterized in this investigation.

⁵ N.m.r. spectra were taken at 56.4 Mc. in diperdeuteromethyl sulphoxide solution; the stability of the adduct in this solvent was established by a control experiment.



followed by a block-diagonal least-squares refinement of positional and isotropic thermal parameters. The discrepancy index R_1 is at present 0.11 for approximately 1200 of the observed reflections. A schematic view of the structural formula of the methoxybromide is given in Figure 1.

Formation of this methoxybromide is readily explained by attack of bromine on the "enamine" double bond of (IV) from the less-hindered side to give a cyclic bromonium ion⁶ which can undergo methanolysis with inversion α to nitrogen. More unusual, however, is the observed conformation (Va) of this substituted 2-azabicyclo[3,2,2]nonene, in which the bromine and methoxyl are held axial and quasi-axial, respectively, and the methoxyl

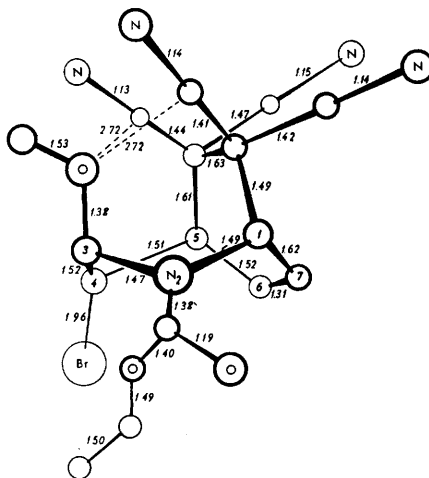
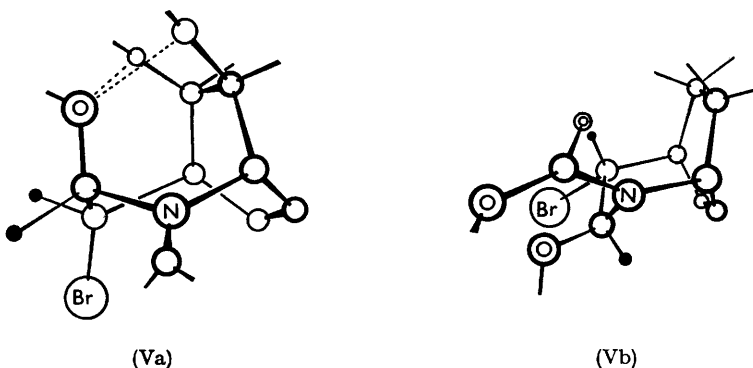


FIGURE 1

oxygen is situated only 2.72 Å equidistant from the two nearest cyano-carbons. The conformation (Va) appears to be preferred over the alternative (Vb) in this particular case because it holds the electrostatic repulsions between the bromine and the methoxyl to a minimum⁷ and simultaneously reduces the steric interference between the three adjacent substituents CO_2Et , OMe , and Br . These conformational arguments are in line with n.m.r. spin-decoupling studies of substituted 2-azabicyclo[3,2,2]nonenes, which will be reported separately.



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⁶ e.g., G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 1954, 4284.

⁷ Compare the preferred diaxial conformation of *trans*-1,2-dibromocyclohexane reported by P. Bender, D. L. Flowers, and H. L. Goering, *J. Amer. Chem. Soc.*, 1955, 77, 3463.