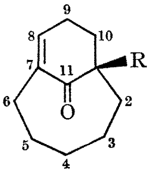
A Distorted Enone: its Structure, Properties, and Reactions†

By G. L. Buchanan,* A. F. Cameron, and G. Jamieson
(*Chemistry Department, University of Glasgow, Glasgow, W.2*)

Summary The spectroscopic and chemical properties of the bicyclo[5,3,1]undec-7-en-11-one derivative (I) are abnormal, and can be interpreted in terms of the geometry of the molecule as revealed by an X-ray crystallographic analysis, carried out on (II).

Bridged bicyclo-compounds can tolerate a bridgehead double bond, in defiance of Bredt's rule[1] up to the limits defined by Fawcett[2] and recently revised by Wiseman.[3] Limiting cases may be expected to show abnormal properties, and we report an examination of such a case (1). Its u.v. spectrum[4,5] [$\lambda_{\max}$ (EtOH) 240 nm; ϵ5630] indicates inefficient overlap of the two π-systems, and in order to measure the distortion, and to discover how the molecule accommodates the strain, the related p-chloranilide (II) has been examined by X-ray crystallography. Crystals of (II) are orthorhombic, space group *Pbca*, $Z = 8$, $a = 19·97$, $b = 7·67$, $c = 21·35$ Å. In all, 983 independent structure amplitudes from the reciprocal lattice nets h 0–8 l were collected on a Hilger and Watts linear diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0·7107$ Å). The position of the chlorine atom was found by Patterson methods and the remaining atoms were revealed by several subsequent electron-density calculations. The atomic parameters were refined initialy by full-matrix and subsequently by block-diagonal least-squares methods to a final value of $R = 0·092$, and the geometry of the relevant part of the molecule is shown in the Figure.



(I) R=CO_2Et
(II) R=CO·NH·C_6H_4·Cl-p
(III) R=H

Molecular strain causes the C=O to be twisted 37·6° about the C(7)–C(11) bond, as seen by comparing the planes through C(6)C(7)C(11) and C(7)C(11)O. The C(7)–C(8) double bond is also twisted by 8·6°, as seen by comparing the planes through C(7)C(8)C(9)—C(6)C(7)C(11). Thus the non-planarity of the enone system is less marked at C(8) than at C(7), but the overall effect is an $\alpha\beta$-enone which is a little better than "half-conjugated". The angle of twist, as calculated from an empirical relationship,[6] is *ca.* 40°, which is surprisingly accurate. Deconjugation also affects bond lengths, and the C(7)–C(8) bond length (1·29 Å) is virtually that of an isolated double bond, whilst the C(7)–C(11) bond (1·48 Å) is as long as the C(1)–C(11) bond (1·49 Å), and thus practically a pure single bond. The average estimated standard deviation for C–C bonds is 0·02 Å, derived from the inverse of the least-squares normal-equation matrix. The effect on the i.r. spectrum is less dramatic. In CCl_4 the enone (I) shows $\nu_{C=O}$ 1736 and 1697 cm.$^{-1}$ with the C=C band appearing only as a shoulder at *ca.* 1690 cm.$^{-1}$. The parent enone (III)[5] gives similar figures (1702 and *ca.* 1690 cm.$^{-1}$) in CCl_4, but in cyclohexane the $\nu_{C=C}$ is clearly visible at 1696 cm.$^{-1}$ with the $\nu_{C=O}$ at 1707 cm.$^{-1}$. Thus unusually high C=C stretching absorption reflects the poor conjugation in the system.

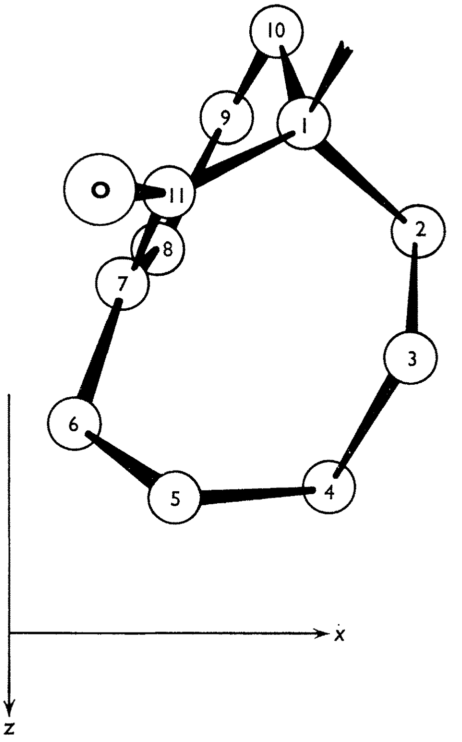


Figure. *A view of the bicyclo*[5,3,1]*undecenone system* (II) *viewed down the* b-*axis. The* p-*chloroanilide function is omitted for clarity.*

Chemically, the enone system is also abnormal. It can be epoxidised, slowly, *either* with m-chloroperbenzoic acid *or* alkaline perhydrol, but to date we have been unable to carry out a Michael addition of malonic ester. More detailed accounts of the structure, properties and reactions of the system will be published later.

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