X-Ray Molecular Structure of a Highly Symmetrical Triketone: [3.3.3]Propellane-2,8,9-trione

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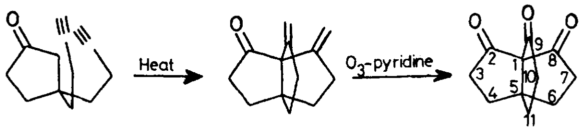
Summary X-Ray analysis of a single crystal of [3.3.3]-propellane-2,8,9-trione (**3**) reveals unexpected attractive interactions between the carbonyl groups.

PROPELLANE derivatives have received considerable attention because of the particular properties of their three-dimentional structures.[1] However, only a few symmetrical propellane derivatives, *e.g.*, triptindane[2] and [3.3.3]propellane-3,7,10-trione,[3] have hitherto been reported.

In the course of our studies on the [3.3.3]propellane series[4a,b] we have prepared the symmetrical [3.3.3]propellane-2,8,9-trione (**3**) by ozonolysis of the dienone (**2**) previously obtained by thermal cyclisation of 3,3-di(but-3-ynyl)-cyclopentanone (**1**).[4b]

A saturated CH_2Cl_2 solution of pure ozone was prepared at −95 °C in Rubin's apparatus[5] to which pyridine was added (1 mol/mol of O_3). The resulting blue solution was added dropwise over a period of 10 min to a CH_2Cl_2 solution of the dienone (**2**) at −95 °C until the blue colour of the added solution just persisted (stoicheiometric amount of ozone). The mixture was allowed to warm up to room temperature. Evaporation of the solvent and recrystallisation of the resulting solid from CH_2Cl_2 gave the triketone (**3**), m.p. 253 °C (decomp.), 50%, ν ($CDCl_3$) 2945w, 2870vw, 1785vs, 1720s, 1220s, 1100vs, 1070m, and 990w cm^{-1}; δ ($CDCl_3$, 250 MHz) A_2X_2 system, δ_A 2·13, δ_B 2·51, J_{AB} 7·8 Hz; m/e 194 (M^+ 100%), 193, 168, 149, 137, 136, 115, 85, 81, 57, and 55.



(1) (2) (3)

In order to establish the steric arrangement of the carbonyl groups in (**3**), an X-ray analysis was carried out on a cubic crystal (CH_2Cl_2) mounted on a four-circle diffractometer (with Cu-K_α radiation monochromatized by graphite).

Crystal data: $C_{11}H_{14}O_3$, M 194, monoclinic, space group $P2_1/c$, $a = 8·514(3)$, $b = 6·881(2)$, $c = 15·964(3)$ Å, $\beta = 101·46(4)°$, and $Z = 4$. The crystal is stable in the X-ray beam. 1846 reflections were scanned in the θ–2θ mode above the background (3σ probability level). The intensities were corrected for Lorentz polarization but not for absorption, and the structure was solved by the combined use of the Riche's phase function[6] and the multisolution method.[7] Among the highest figures of merit, the fourth was found to contain correct atomic positions for two of the three rings of the molecule. The *F* recycling procedure therefore allowed the whole structure to be developed. After subsequent full-matrix least-squares refinement of the atomic positional parameters and anisotropic thermal factors, the final *R* index was 4·7%. All the hydrogen atoms were located on difference Fourier synthesis and their positions were refined. The final view of the molecule together with bond lengths and bond distances is shown in the Figure.†

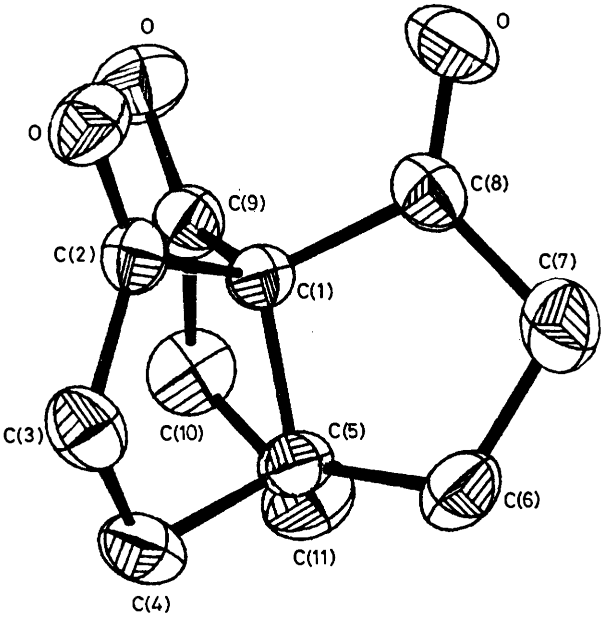


FIGURE. ORTEP diagram of the molecular structure of (**3**). Bond distances (±0·005 Å) and angles (±0·10°) are: C(1)–C(2), 1·537; C(2)–O, 1·201; C(1)–C(5), 1·523; C(2)–C(3), 1·510; C(3)–C(4), 1·515; and C(4)–C(5), 1·540 Å; ∠C(5)–C(1)–C(2), 106·6; ∠C(1)–C(2)–C(3), 107·7; ∠C(1)–C(2)–O, 125·0; ∠C(3)–C(2)–O, 127·4; ∠C(2)–C(1)–C(8), 111·6; and ∠C(4)–C(5)–C(6), 114·0°.

The *X*-ray analysis clearly shows the lack of repulsive interactions between the keto-groups. Moreover, the C(1)–C(2)=O and C(3)–C(2)=O angles reveal weak attractive interactions, while the C(5)–C(1)–C(2)=O dihedral angle is 174° (*cf.* cyclopentanone, 150°) which brings the oxygen atoms closer to each other.

The photoelectron spectrum of (**3**) [I.P. at −9·35 and −9·85 (±0·05) eV][8] shows couplings between the *n* orbitals of the oxygen atoms, the energy level separation being 0·50 eV. This value can be compared with the 0·81 eV splitting calculated for a model 1,3-dione with parallel carbonyl groups 3·6 Å apart.[9] The O–O distance in (**3**) is 3·2 Å and the geometry of (**3**) should permit only a smaller interaction. Overlapping of the $\pi_{C=O}$ and σ bands prevents further information being obtained; nevertheless, these overlappings probably resemble those of the $\pi_{C=C}$ orbitals of the 2,8,9-trimethylene[3.3.3]propellane [I.P. at −8·90, −9·16, and −9·50 (±0·10) eV][9] for which the energy level separation reaches 0·43 eV.

We conclude that the increased tendency of this structure towards overlap of *n* and/or $\pi_{C=O}$ orbitals has a stabilizing effect which is probably reflected in the shortening of C=O distance to 1·201 Å (cyclopentanone,[10] 1·226; $\alpha\beta$-enones,[11] 1,207 Å).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table may be obtained as a supplementary publication (No. 22104, 12 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, Index Issues of *J.C.S. Perkin I* or *II*, 1976.

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