X-Ray Structure of the 1,2-Dioxetan Dispiro(adamantane-2,3′-[1,2]dioxetan-4′,2″-adamantane)

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Summary X-Ray data for dispiro(adamantane-2,3′-[1,2]-dioxetan-4′,2″-adamantane) are presented and support suggestions regarding the reasons for its unusual stability.

THE chemiluminescent decomposition of 1,2-dioxetans is the subject of continuing study.[1,2] Structural parameters can be helpful in substantiating the proposed reason[3] for the unusual stability of the dispiro-1,2-dioxetan (I).[4] X-Ray data for this class of compounds will be useful in any careful evaluation of the steric requirements of 1,2-dioxetans in bioluminescent systems.[5] Our own need for these data is evident from our recent studies.[2] We therefore report the X-ray crystal structure of dispiro(adamantane-2,3′-[1,2]dioxetan-4′,2″-adamantane) (I).

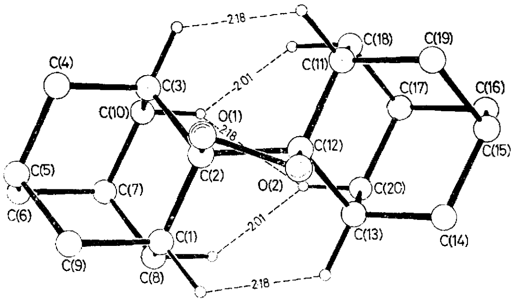


FIGURE 1. The molecule of (I) seen along the line connecting the centres of O(1)–O(2) and C(2)–C(12), with short non-bonded distances. In addition to the distances shown, the distances of type C(1) ··· C(13), 3·14 Å, are shorter than the sum of the van der Waals radii (3·4 Å) (ref. 8).

Crystal data: $C_{20}H_{28}O_2$, monoclinic, space group $P2_1/c$, $a = 18{\cdot}59(1)$, $b = 9{\cdot}89(1)$, $c = 13{\cdot}24(1)$ Å, $\beta = 105{\cdot}3(1)°$, $D_m = 1{\cdot}27$, $D_c = 1{\cdot}28$ g cm^{-3}, $Z = 6$. The structure was solved by direct methods. One set of four molecules lies at a general position; the remaining two molecules lie at inversion centres and are disordered. $R = 0{\cdot}11$ for 2164 reflections, which could not be measured very accurately owing to slight decomposition. The structure of the molecule is given in Figures 1 and 2. The length of the O–O bond, 1·48 Å, is equal to that in H_2O_2.[6] The average length of the C–C bonds in the adamantyl groups is 1·531 Å, whereas the central C–C bond has a length of 1·549 Å. In view of the standard deviation of 0·009 Å this elongation is not significant. The C–O bond length of 1·475 Å is definitely longer than the value of 1·423 Å observed in 1,4-dioxan.[7] The oxygen-containing four-membered ring is non-planar (see Figure 2). Although the rotation around the central C–C bond is such that the shortest H ··· H distances shown in Figure 1 are enlarged, they are still shorter than the value of 2·4 Å given by Pauling[8] for van der Waals H ··· H distances.‡

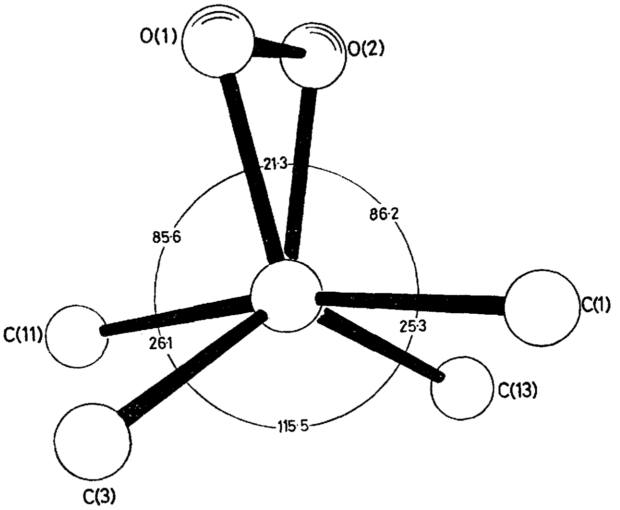
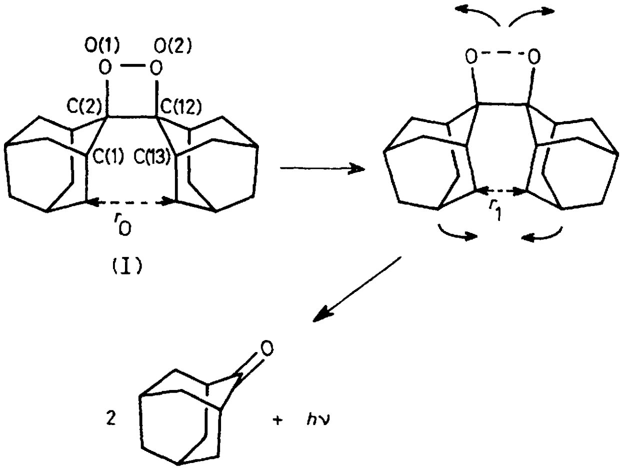


FIGURE 2. The molecule of (I) seen along C(2)–C(12), with torsion angles.

The *X*-ray structure of (I) cannot of course by itself prove its decomposition mechanism. Two decomposition modes are feasible. A planar, non-torsional mode[3] is pictured in the Scheme in which a stretching of the O–O bond is coincident with a compression of the two adamantyl substituents. A second mode[9] involves a concerted torsional decomposition as the two adamantane units appear to 'unscrew.'



SCHEME. Planar, non-torsioanl decomposition mode of (I).

In the *X*-ray data of (I) the closest separations of the pertinent hydrogen atoms are shorter than the Van der Waals H ··· H distance. Knowing this, it seems reasonable that the first mode of decomposition has a relatively high energy barrier, owing to the difficulty of compressing the adamantyl groups closer to one another. In the second mode this type of steric hindrance is not present. If (I) decomposes in this manner, as proposed by Turro *et al.*,[9] the stability of (I) may be due to a high energy barrier arising from the large inertial masses of the rigid adamantane units.

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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.

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