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The structure of anti-tricyclo $|4.2.2.0^{2.5}|$-deca—3,9-diene-7,8-endo-dicarboxylic anhydride

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Chimica fisica. — *The structure of anti-tricyclo* $|4.2.2.0^{2.5}|$ *-deca-3,9-diene-7,8-endo-dicarboxylic anhydride.* Nota di GIUSEPPE FILIPPINI e MASSIMO SIMONETTA, presentata (*) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — È stata determinata mediante diffrazione di raggi X e impiego dei metodi diretti la struttura cristallina e molecolare dell'anidride anti-triciclo $|4.2.2.0^{2.5}|$ deca-3, 9-dien-7,8-endo-dicarbossilica.

The conformation and the reactivity of bicyclo [2.2.2] octane and its derivatives is a subject of considerable interest and discussion [1, 2].

In the sequence of studies undertaken in our Laboratory, the structure of anti-tricyclo [4.2.2.$o^{2.5}$]-deca-3,9-diene-7,8-endo-dicarboxylic anhydride has been determined by X-ray diffraction.

Crystals of the substance (m.p. 167°) were obtained by Diels-Alder reaction of cyclooctatetraene with maleic anhydride [3]. They are monoclinic, space group $P2_1/c$, with $a = 6.385$ ($\pm$ 0.001), $b = 21.922$ ($\pm$ 0.002), $c = 6.622$ Å ($\pm$ 0.001), $\beta = 91.76°$ ($\pm$ 0.02°) and four molecules per unit cell. These data were obtained by Cohen's back reflection method, as described by Buerger [4], using CuK_α radiation ($\lambda_1 = 1.54051$, $\lambda_2 = 1.54433$ Å) at a room temperature of 21° C. The effective radius of the camera (an ordinary Weissenberg) was determined by mounting the film according to the Straumanis technique. The standard deviations were taken from the sum of the residuals, according to Whittaker and Robinson [5].

The measured density is 1.44 g cm^{-3} and the corresponding calculated value is 1.448.

The structure was solved by direct methods and refined by least-squares.

At the present stage of the refinement, the R index is 0.123 on 579 observed independent reflections with intensity greater than twice their e.s.d. Anisotropic temperature factors for carbon and oxygen atoms were used in the last cycles of least-squares. The uncertainty of the bond distances does not exceed 0.025 Å and of bond angles 1.5°: the most salient details of the molecular geometry are reported in fig. 1. The molecular symmetry (non crystallographic) is close to m.

In the bicyclo-octene nucleus, most of the angles centered on sp^3 carbon atoms are almost tetrahedral. The angles C(2)—C(1)—C(8) and C(5)—C(6)—C(7) are somewhat smaller than normal; the angles centered on sp^2 carbon atoms C(9) and C(10) are showing a significant deviation from 120°. All these values, however, are very close to the corresponding bicyclo [2.2.2]-oct-5-ene-2,3-endo-dicarboxylic anhydride[1] and bicyclo [2.2.2] octane-

(*) Nella seduta del 12 dicembre 1970.

1,4–dicarboxylic acid [6] data. The bond distance C(2)—C(5) is significantly longer than usual: other examples of this kind can be found in strained molecules such as tricyclo [5.2.1.$o^{2,6}$]–deca–4,8–dienyl–*p*–bromobenzoate [7] and dichlorobenzocyclobutene [8].

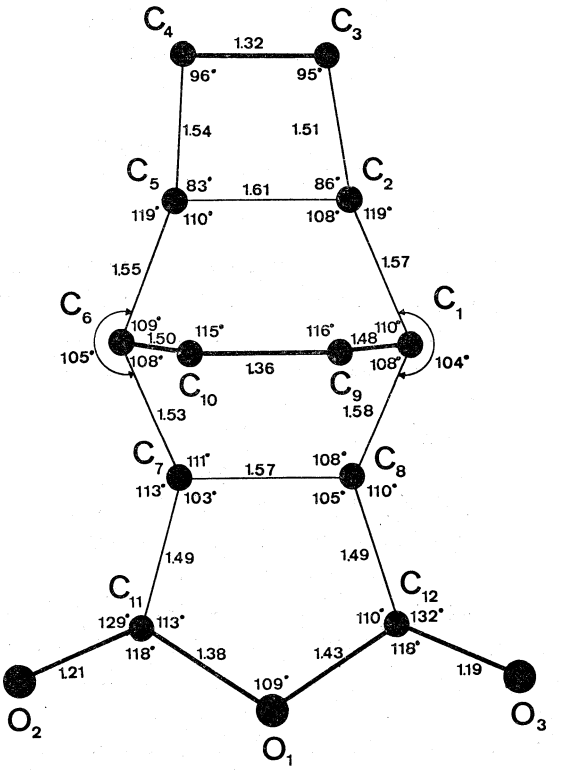

Fig. 1. – Bond distances and angles in anti-tricyclo 4.2.2.$o^{2,5}$ deca–3,9–diene–7,8–endo–dicarboxylic anhydride. The molecule is seen along the direction corresponding to the maximum moment of inertia.

The atoms C(2), C(3), C(4), C(5), which form the butene ring, are coplanar within the experimental uncertainty (P1); the same situation occurs for the other three planes (P2 , P3 , P4) defined by the atoms C(1), C(6), C(9), C(10), the atoms C(1), C(2), C(5), C(6) and the atoms C(1), C(6), C(7), C(8) respectively, which form the bicyclo-octene nucleus. This excludes any significant twisting from ' eclipsed ' configuration around the C(1)–C(6) axis.

The geometry of the anhydride group is close to the situation observed for similar compounds [1]. The atoms C(7), C(8), C(12), O(1) and C(11) are coplanar within the range of experimental error.

The dihedral angles between the P3 and the P1 and P2 planes are 119° and 124° respectively; the ones between the P4 plane and the P2, P3 planes and the anhydride ring are 122°, 114°, and 120° respectively.

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