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THE CRYSTAL AND MOLECULAR STRUCTURE OF 3,11,14,22-TETRA-*t*-BUTYLDIDEHYDRO[22]ANNULENE

Chizuko Kabuto and Yoshio Kitahara†
Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980, Japan
Masahiko Iyoda and Masazumi Nakagawa
Department of Chemistry, Faculty of Science, Osaka University
Osaka 560, Japan

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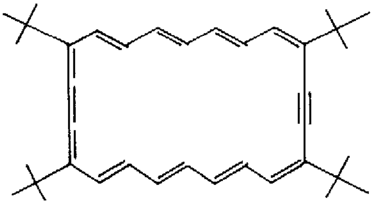
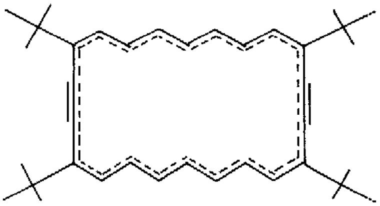
As an extension of the structural studies of didehydro[14]annulene (1)[1] and tetra-*t*-butyldidehydro[18]annulene (2)[2], we have undertaken the X-ray crystallographic study of tetra-*t*-butyldidehydro[22]annulene (3), which had been found to sustain a diamagnetic ring current[3]. It was the intention of this study to determine whether the symmetrical structure, similar to the cases of (1) and (2), would hold true or not in the 22-membered system.

This compound belongs to the space group $P2_1/n$ with the cell dimensions of a=14.566, b=17.163, c=14.037 Å and β=106.79°. The calculated density, based on four molecules per unit cell, is 1.00 g/cm^3. It should be noted that this evidence is different from the cases of (1) and (2) in which the unit cell contains two molecules, implying the absence of crystallographically rigorous symmetry required of the structure because the molecule occupies a general position.


(Ia)


(Ib)

A single crystal with the dimensions of 0.25x0.25x0.3mm was sealed in a thin-walled glass capillary and used to the intensity measurements. A total of 5320 reflections were collected, of which 3290 reflections were coded as observed. Three standard reflections, which were monitored every 60 reflections, showed a slow decomposition of the crystal; the final intensities dropped to 85% of the initial values. Each of the intensities was modified in a common scale using the check reflections

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† Deceased, Feb. 4th, 1976

The structure was determined by the direct method and refined by the block-diagonal least-squares method using all reflections except for unobserved ones with $\sin\theta/\lambda > 0.45$. The positional and anisotropic temperature factors of the 38 C atoms were refined until the R-factor had dropped to 0.15. A difference map at this stage revealed clearly the locations of the 14 H atoms which were bonded directly to the ring and then all of them were included in the successive refinement. Additional difference map was calculated, which did not located unambiguously but disorderly the hydrogen atoms of the methyl groups.
No attempt was made to include the 36 H atoms in further calculations. Refinement was terminated to give an R-factor of 0.12 for all non-zero reflections.

The molecular structure of (3) is shown in Fig. 1. The bond lengths and angles within the 22-membered ring skeleton are obtained to be well-refined, although the positions of the methyl carbon atoms involve the large uncertainty. It is apparent that the structural symmetry expected from the formula [Ib] is destroyed more or less by the bond lengths. An appreciable difference is seen between the two straight linkages in which sp-hybridized carbon atoms participate to form bonds; that is, the lengths of C(2)-C(1)-C(22)-C(21) are 1.400, 1.186, and 1.404 Å, while the lengths of C(10)-C(11)-C(12)-C(13) are 1.370, 1.216 and 1.370 Å. These systematic changes must reflect that the former linkage has relatively more acetylenic bond character, while the latter more cumulenic. Simultaneously, the succession of long and short bonds can be seen also in the polyene parts. The eight bond, which are assigned to be longer are in the lengths of 1.379-1.409 Å, while the other shorter ones are in the lengths of 1.366-1.389 Å, and the average lengths are 1.397 and 1.377 Å, respectively. The difference of length between the long and short bonds can't be taken as significant for the experimental error. It is, however, pointed out that the bonds of C(10)-C(9) and C(13)-C(14), neighbouring to "cumulenic" linkage, indicate an enhanced single bond character, on the other hand, the bonds of C(2)-C(3) and C(21)-C(20), neighbouring to "acetylenic", double bond character. Thus, at either event the pattern in the lengths consistently lead to the conclusion that the alternate bond structure such as [Ia], apart from the extent, appears in the case of the 22-membered system. On the other hand, the lower 14- and 18-membered systems are found to have a fully delocalized π-bond structure.[1,2] These evidences, therefore, should be the experimental support to justify the theoretical prediction that the bond alternation in annulenes should increase with the increase of the ring size.[4] Furthermore it might be said that the present observation on the structure is responsible for the result of nmr spectrum that the diatropicity of (3) is less than those of (1) and (2).[5,6,7]

Fig. 2 shows the deviations of atoms from the best plane through the 22 ring carbon atoms. It is also apparent that this macrocyclic ring skeleton shows a fairly distortion from the coplanarity, as opposed to the planar conformation in (1) and (2).

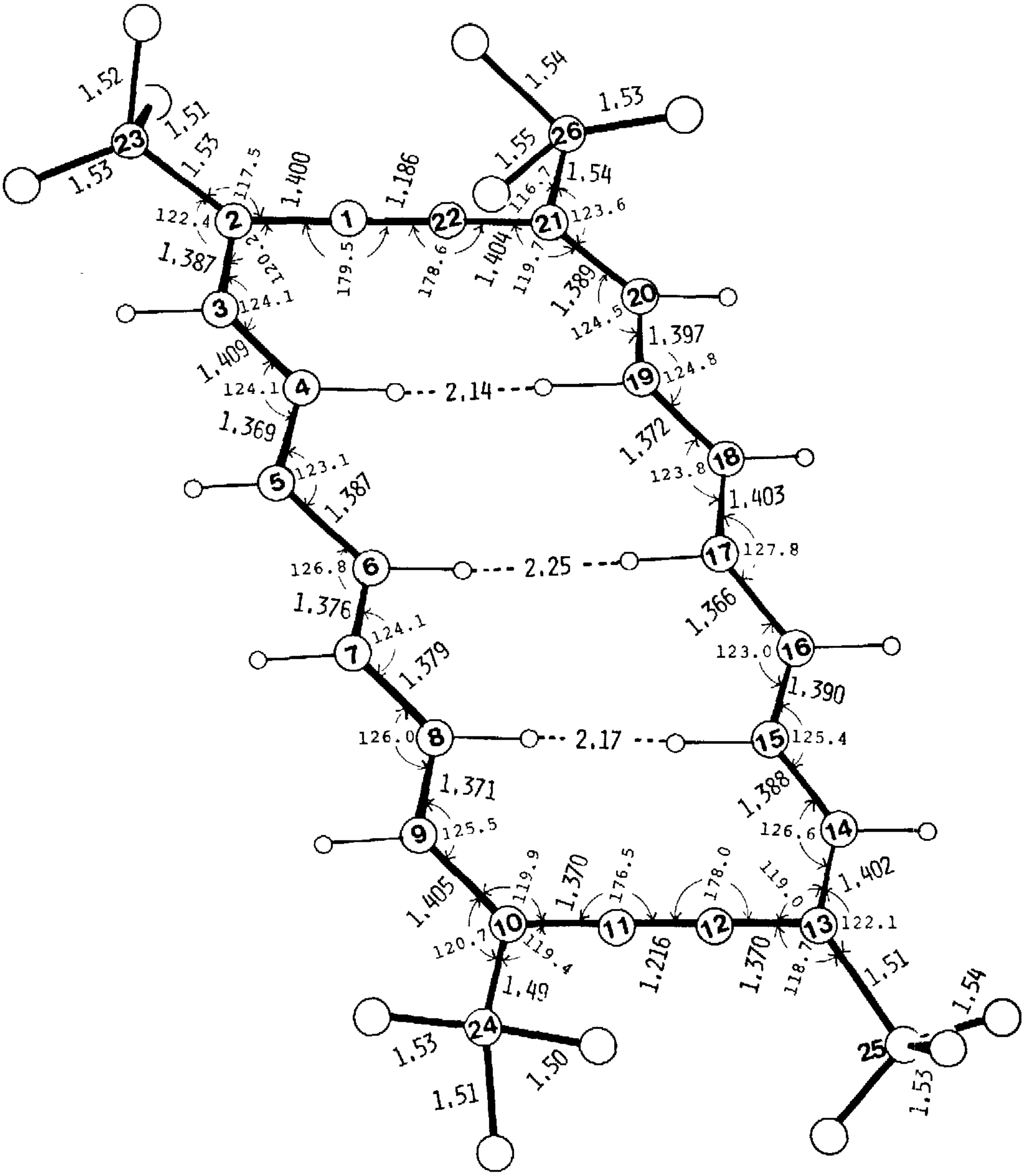

Fig.1. Bond lengths and bond angles of (3). The standard deviations are as follows: 0.6-0.8° in the bond angles, 0.008-0.009 Å in the innercyclic C-C bond lengths, 0.009-0.011 in the exocyclic ones, and 0.012-0.014 Å in the methyl C-C bond lengths. C-H bond lengths are 0.98-1.03 Å

Suprisingly, the skeleton appears to be slightly bent down from the half line across the ring, as indicated by the deviations that the central atoms C(6) and C(17) lie above 0.143 and 0.154 Å from the plane, while the four corner atoms C(2), C(10), C(13) and C(21) lie down 0.045, 0.162, 0.208 and 0.247 Å, respectively.

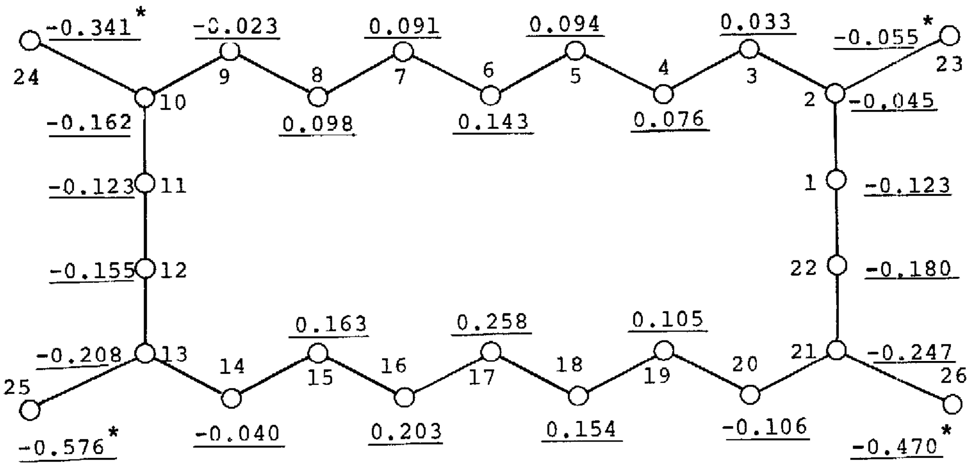

Fig. 2. The deviations of atoms (Å) from the least-squares plane through the ring carbon atoms. The exocyclic carbon atoms are not included in the plane.

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