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MANIFESTATION OF A (DISTORTED) TRIGONAL PYRAMIDAL STRUCTURE OF A QUADRIVALENT CARBON

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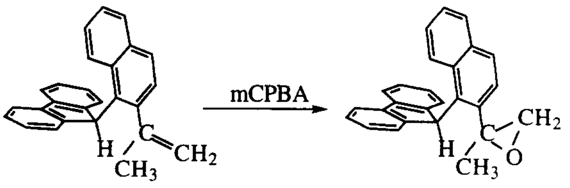
Abstract: Reactions of *ap*- and *sp*-rotamers of 1-(9-fluorenyl)-2-(1-methylethenyl)-naphthalene with *m*-chloroperoxybenzoic acid afforded the corresponding epoxides. Of these, the *ap*-epoxide was found to contain a carbon atom, the structure of which is a distorted trigonal pyramid, the carbon atom being located close to the center of the base triangle. © 1997 Elsevier Science Ltd.

A carbon atom is known to normally take a tetrahedral structure if it is quadrivalent. There are two elusive structures of carbon, a tetragonal pyramid and a trigonal pyramid. The tetragonal pyramid, the apex of which is occupied by a carbon atom and the basal positions by substituents has been assumed as one of the possibilities of the quadrivalent carbon in classical stereochemistry. 1) The trigonal pyramid structure has attracted little attention of chemists, although this structure is also capable of accommodating the chiral nature of the carbon atom which is substituted by four different groups.

If we can introduce lithium atoms in place of hydrogens, calculations show that there can be odd-shaped carbons and silicons. Schleyer and coworkers have shown by calculation that a C_{2v} structure is most stable for tetralithiosilane 2) and a planar structure is preferred for tetralithiomethane. 3) However, to the best of our knowledge, none of the examples of these queer-shaped molecules has been synthesized, although trigonal bipyramid structures are reported for carbon atoms. 4,5) During the course of examining the reactivities of 9-arylfluorene rotamers, we encountered an example in which a quadrivalent carbon atom is



ap-**1** *sp*-**2**

sp-**1** *ap*-**2**

located nearly at the center of a triangle and the fourth substituent up on the triangle. The carbon atom is an oxiranyl carbon in *ap*-1-(fluorenyl)-2-(2-methyl-2-oxiranyl)naphthalene. We wish to report the results of our study in this paper.

The epoxidation of *ap*-**1** and *sp*-**1** was carried out with ca. 2 equivalents of *m*-chloroperoxybenzoic acid (mCPBA) in dichloromethane at room temperature. The reaction was completed within 20 h for both isomers. The reactions were clean and produced the corresponding epoxides (**2**) in over 80% yields. 6,7)

It was a great surprise for us to find that both *sp*- and *ap*-1-(9-fluorenyl)-2-(1-methylethenyl)naphthalenes (**1**) reacted smoothly with mCPBA to afford the corresponding oxirane (**2**) for the following reasons. During the study of the reactivity of rotational isomers of 1-(9-fluorenyl)-2-(1-methylethenyl)naphthalene (**1**) with various reagents, we successfully explained the results by assuming that only an open cation is produced when a cationic species, such as a halogen cation, attacks the olefinic moiety of the molecule due to the steric effects, whereas the 3-membered ring halonium ions can be formed from the *ap*-isomer: 8–10) If a tetrahedral arrangement of the carbon in the ethenyl moiety is required in the reaction for the *sp*-form, the steric effects 11) are too severe, thus impeding the reaction.

In order to understand the underlying reasons for the facile reaction of *sp*-**1** with mCPBA, we performed X-ray crystallography of *ap*-**2**. The results are shown as an ORTEP drawing in Fig. 1 and some of the relevant data in Table 1. 10) The most intriguing feature of the structure is that the oxirane carbon (1"), which is connected to the naphthyl carbon, forms three bond angles of almost 120 °: C(2')–C(1")–C(2"), C(2')–C(1")–C(3"), C(2")–C(C1")–C(3"). That is, a plane made by the three carbon atoms (C2', C2", and C3") almost exactly includes the carbon atom of the oxirane ring. In accord with this feature are the short C–C bond lengths involving the oxirane carbon, C(1")–C(2'), C(1")–C(2"), C(1")–C(3"). These bond angles and the bond lengths indicate that the central carbon is close to the sp^2 hybridized state. In accordance with this hybridization, the C(1")-O bond is long, whereas the C(2")–O bond is short. Thus, this carbon C(1") takes a distorted trigonal pyramid structure.

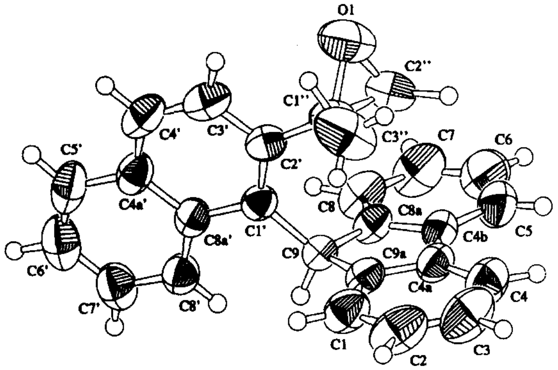


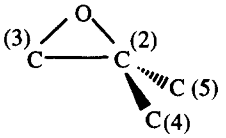
Fig. 1. ORTEP drawing of *ap*-**2**

The Cambridge Crystallographic Data Centre file contains 118 compounds that carry an oxirane ring in which one of the carbon atoms carries two carbon substituents whereas the other carries only hydrogens (see **3**). The data are widely scattered except for the bond length of C(3)–O in **3**.

Table 1. Selected Bond Lengths and Bond Angles in *ap*-**2**

Atom-Atom	Bond Length /Å	Atom-Atom-Atom	Bond Angle/°
C(1")–C(2')	1.505(5)	C(2')–C(1")–C(2")	120.1(3)
C(1")–C(2")	1.490(6)	C(2')–C(1")–C(3")	118.4(3)
C(1")–C(3")	1.469(6)	C(2")–C(1")–C(3")	119.7(3)
C(1")–O	1.487(5)	C(2")–C(1")–O	55.8(2)
C(2")–O	1.394(6)	O–C(2")–C(1")	62.0(3)
		C(1")–O–C(2")	62.2(3)
		O–C(1")–C(2')	112.4(3)
		O–C(1")–C(3")	111.8(3)

The C(4)–C(2)–C(5) angles, which correspond to C(2')–C(1")–C(3") in *ap*-**2**, are in the range of 89.5–120.9° , the median value being 114.2°. The C(4)–C(2)–C(3) angles are in the range of 112.4–131.7°. the median value being 121.6°, while the C(5)–C(2)–C(3) angles from 113.6 to129.2°, the median value being 119.9°. Thus, the bond angles involving the oxirane ring can be said to tend to have wider angles than normal sp^3-hybridized carbons. However, the general structure suggests that at least one bond angle involving the C(2) in **3** is significantly smaller than 120° and the carbon atom C(2) is lifted from the plane made by C(3), C(4), and C(5).



3

As to the bond lengths in the oxirane ring, the following has been noticed. The C–C bond within the oxirane frame is from 1.404 to 1.571 Å, the median value being 1.464 Å. The longest bond is far apart from bonds in other compounds and is an exception. The C(3)–O bonds are from 1.331 to 1.717 Å. Again the longest bond is an exception and the median value is 1.446 Å. The C(2)–O bond lengths are from 1.491 to 1.377 Å, the median value being 1.444 Å. Comparing these values with the present data, we notice that the C(1")–C(2") bond in *ap*-**2** is a little longer than the normal one, the C(2")–O bond is significantly short, and C(1")–O bond significantly long.

As to the carbon-to-carbon bonds, the median bond length of C(2)–C(3) in **3** is 1.464 Å, that of C(2)–C(4) 1.521 Å, and C(2)–C(5) 1.505 Å. Probably, we must take into account that, in compound *ap*-**2**, the C(1")–C(2') bond should be shorter than the median value because the C(2') is an sp^2-hybridized carbon. Generally speaking, however, we notice that the bonds in compound *ap*-**2** are shorter than the median values. This will mean that the sp^2-like hybridization of the C(1") atom is responsible for these bond lengths.

Although the general structure of the oxirane ring suggests that the C–C(2)–C bond angles in **3** can be fairly easily distorted from the normal tetrahedral value, this planar structure should be unstable in a general sense. We have sought the reasons for the carbon to take such a structure. Of course, one of the reasons could be that the π-system of the fluorene ring participates from the back side of the O–C(1") bond to stabilize the planar carbon, the situation being found in the trigonal bipyramid structure.[4,5)] However, this kind of assistance of the π-system is unlikely because the nonbonding distance between the π-system of the fluorene and the C(1") is more than 3 Å, which is too long for claiming a bond, though charge transfer interaction might be possible. Furthermore, thermal equilibration of *sp*-**2** and *ap*-**2** in a boiling toluene solution afforded the equilibrium constant of 19/1 in favor of the *sp*-form of **2** relative to *ap*-**2**. These facts indicate that there does not exist any special stabilizing factor for *ap*-**2**.

The present study reveals that the reason for the existence of the distorted trigonal pyramid structure of a carbon atom should be at least partially attributed to the facile distortion of the bond angles in the oxirane ring. Probably the same reason applies to the facile formation of the oxirane from *sp*-**1**, irrespective of its being at the congested site. Further study to seek the reasons for this unusual structure for a quadrivalent carbon and possible extensions of the finding to a general principle for manifestation of this interesting structure is in progress.

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6. *ap*-**2** gave satisfactory results of elemental analyses: mp 142-143 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.71$ (3H, d, $J = 0.6$ Hz), 1.63 and 1.78 (2H, ABq, $J = 4.5$ Hz), 6.31 (1H, s), 7.14-7.31 (4H, m), 7.40-7.46 (2H, m), 7.60 (1H, d, $J = 8.5$ Hz), 7.60 (1H, ddd, $J = 1.2$, 6.8, and 8.0 Hz), 7.68 (1H, ddd, $J =$ 1.6, 6.8, and 8.4 Hz), 7.85 (1H, d, $J = 8.8$ Hz), 7.89 (2H, dd, $J = 1.7$ and 7.7 Hz), 7.96 (1H, dd, J = 1.5 and 8.0 Hz), 8.63 (1H, d, $J = 8.7$ Hz).
7. *sp*-**2** gave satisfactory results of elemental analyses: mp 133-134 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.91$ (3H, s), 3.15 and 3.24 (2H, ABq, $J = 5.2$ Hz), 5.93 (1H, s), 6.42 (1H, d, $J = 8.6$ Hz), 6.84 (1H, ddd, J = 1.4, 6.9, and 8.6 Hz), 7.06 (1H, d, $J = 6.9$ Hz), 7.16-7.24 (4H, m), 7.40-7.45 (2H, m), 7.72 (1H, d, $J = 8.1$ Hz), 7.73 and 7.82 (2H, ABq, $J = 8.2$ Hz), 7.97 (2H, dd, $J = 0.9$ and 7.6 Hz).
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12. Crystallographic data are as follows. Empirical formula $C_{26}H_{20}O$, formula weight 348.44, crystal dimensions $0.38 \times 0.13 \times 0.45$ mm^3, crystal system monoclinic, lattice parameters a = 12.580(3) Å, b = 8.608(2) Å, c = 17.426(1), β = 95.02(1)°, V = 1879.9(5) Å^3, space group $P2_1/n$, Z = 4, D_{calc} 1.231 g/cm^3, $\mu(CuK\alpha)$ 5.65 cm^{-1}, R 0.068, R_w 0.057.

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