

The Crystal and Molecular Structure of a Trimer Diketone from the Reaction of 7-*tert*-Butoxynorbornadiene with Iron Pentacarbonyl

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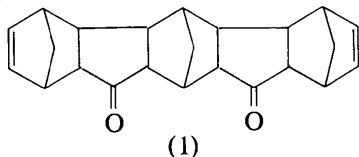
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The highly stereospecific reaction of 7-*tert*-butoxynorbornadiene, a strained olefin, with iron pentacarbonyl produces at least five products. For one of these, *anti,anti,anti*-13,14,15-tris(1,1-dimethylethoxy)-1,4:6,12:7,10-trimethano-1,4,4a,5a,6,6a,6b,7,10,10a,11a,12,12a,12b-tetradecahydroindeno[1,2-*b*]fluorene-5,11-dione, C₃₅H₄₈O₅, the structure has been determined using three-dimensional X-ray diffraction data and refined to a final *R* value of 6.8% for all 6520 data with $2\theta < 150^\circ$. The data were measured from a single crystal using a Nonius CAD-4 automatic diffractometer and Cu *K* α radiation. The compound crystallizes in the monoclinic space group *P*2₁/*c*, *Z* = 4, with *a* = 10.5378 (8), *b* = 27.084 (3), *c* = 12.7897 (6) Å and β = 120.928 (5)° at a temperature of 24°C. In total, there are 2304 different ways in which three 7-*tert*-butoxynorbornadiene residues can couple with alternating C=O groups. The fact that only one of these possible products is formed in the chemical reaction demonstrates the stereospecificity of the coupling mechanism. An observed shortening of the bond distance connecting the O atom to the 7 position of the norbornadiene residue is ascribed to a hybridization effect.

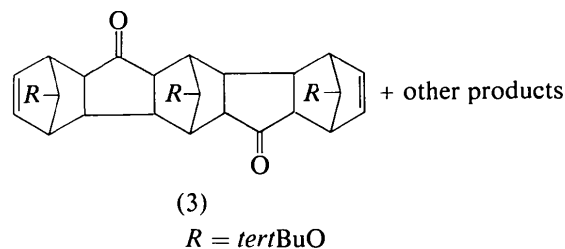
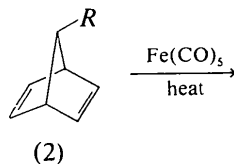
Introduction

Some years ago, Cookson and coworkers studied the thermal reaction of norbornadiene with iron pentacarbonyl (Bird, Cookson & Hudec, 1960). Three ketonic products were isolated from this reaction. One of these ketones, m.p. 218°C (decomposition), was found to be C₂₃H₂₄O₂ on analysis. A linear trimeric diketone structure (1) was suggested for this material. However, to our knowledge, no detailed account of the proof of structure (1) has appeared, nor has any direct method (X-ray crystallography, electron or neutron diffraction) been applied to verify this structural assignment.



We recently examined the thermal reaction of 7-*tert*-butoxynorbornadiene (2) with iron pentacarbonyl. A ketonic material (3), m.p. 226–227°C, was isolated from this reaction (along with other products). The molecular formula of this material was established as being C₃₅H₄₈O₅ *via* mass spectral analysis and elemental microanalysis (see *Experimental*). However, as was found to be the case with the other products isolated from this reaction (Neely, van der Helm, Marchand & Hayes, 1976), the structure of (3) could not be unequivocally established by conventional spectroscopic techniques (NMR, infrared, and mass spectra). Accordingly, we turned to single-crystal X-ray diffrac-

tion analysis in an effort to provide conclusive proof for the structure of (3).



Experimental

Melting points are uncorrected. NMR spectra were obtained on a Varian XL-100-15 spectrometer (CDCl₃ solvent, TMS internal standard). Infrared spectra were obtained on a Beckmann IR-8 infrared spectrophotometer (KBr pellet). Mass spectra were obtained at 10 eV on a Hitachi-Perkin Elmer RMU 7E mass spectrometer.

The conditions for the thermal reaction of (2) (10.0 g, 61.0 mmol) with iron pentacarbonyl (25.00 g, 127.5 mmol) have been described elsewhere (Neely, van der Helm, Marchand & Hayes, 1976). Isolation

and purification of the various reaction products were accomplished *via* elution chromatography on TLC grade silica gel (100 g, manufactured by E. Merck, AG, Darmstadt, W. Germany, column dimensions 4 × 50 cm, 1:9 ethyl acetate–hexane eluant). The first product to be eluted from the column (14%) was a cage dimer (Neely, van der Helm, Marchand & Hayes, 1976); the second (25%) was a dimeric ketone (Ealick & van der Helm, 1975*b*). The third product to be eluted (19%) was a colorless crystalline solid. Recrystallization of this material from pentane (−78°C) afforded pure (3), m.p. 226–227°C. Proton NMR spectrum (CDCl₃): δ6.1 (mult, 4H, 2-, 3-, 8-, 9-protons), δ3.70, 3.56, 3.46 (mults, 3H, 13-, 14-, 15-protons), δ3.04, 2.82, 2.70 (mults, 4H, 4a-, 5a-, 10a-, 11a-protons), δ2.48, 2.31, 2.18, 2.07 (mults, 6H, 1-, 4-, 6-, 7-, 10-, 12-protons), δ1.98, 1.61 (mults, 4H, 6a-, 6b-, 12a-, 12b-protons), δ1.12, 1.11, 1.10 [s, 9H, −OC(CH₃)₃]; infrared spectrum (KBr pellet): 3060(*w*), 2980(*s*), 1722(*s*), 1458(*m*), 1390(*m*), 1362(*m*), 1253(*m*), 1190(*s*), 1023(*w*), 900(*m*), 692(*m*) cm^{−1}; mass spectrum (10 eV), *m/e* (% of base peak) 548 (parent ion, 2%), 298 (9), 91 (20), 82 (37), 57 (100), 41 (19).

Analysis calculated for C₃₅H₄₈O₅: C, 76.66; H, 8.75%. Found (Chemalytics, Inc.): C, 76.56; H, 9.07%.

Large single crystals of the title compound were obtained by slow evaporation from acetone. The crystal used for the diffraction experiment was cut to a more suitable size (0.52 × 0.26 × 0.17 mm) from one of the larger crystals. Integrated intensity data and crystallographic data (Table 1) were obtained from measurements made on a Nonius CAD-4 automatic diffractometer. For the intensity data Ni-filtered Cu K $\bar{\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used and for the determination of unit-cell parameters Cu K α_1 radiation ($\lambda = 1.54051 \text{ \AA}$) was used. 6520 intensities, comprising all the unique data of the type $\pm hkl$ with $2\theta \leq 150^\circ$, were measured using θ – 2θ scan techniques, and a variable scan width calculated as $(1.1 + 0.11 \tan \theta)^\circ$. A receiving aperture with variable width calculated as $(4.0 + 0.86 \tan \theta) \text{ mm}$ and a constant height of 6.0 mm was located 173 mm from the sample. The maximum time spent on each measurement was 60 s

Table 1. Crystallographic data

The cell dimensions were determined by least-squares fit to the $+2\theta$ and -2θ values of 56 reflections ($40^\circ < 2\theta < 86^\circ$) centered at 24°C.

Formula: C ₃₅ H ₄₈ O ₅	$\beta = 120.928 (5)^\circ$
$M_r = 548.73$	$V = 3131.2 \text{ \AA}^3$
Space group: $P2_1/c$ (No. 14)	$Z = 4$
$a = 10.5378 (8) \text{ \AA}$	$\rho_{\text{calc}} = 1.164 \text{ g cm}^{-3}$
$b = 27.084 (3)$	$\rho_{\text{obs}} = 1.162$
$c = 12.7897 (6)$	(determined by flotation in aqueous KI solution)

with 40 s used for scanning the peak and 10 s used for scanning each of the left and right backgrounds. If 50 000 counts could be obtained in less than 60 s a faster scan speed was used. A total of 401 reflections were considered indistinguishable from the background having $I \leq 2\sigma(I)$ and were assigned an intensity of 1.4 times the total count for the purpose of further data analysis. A monitor reflection was measured after every 30 reflections and showed no significant decrease at the end of the data collection. Three orientation control reflections were centered after every 200 observations. In the event of any angles differing by more than 0.1° a new orientation matrix would have been automatically determined. Lorentz and polarization corrections were applied and individual structure factor amplitudes derived but absorption corrections ($\mu = 6.09 \text{ cm}^{-1}$) were not made. Each

Table 2. Positional parameters ($x, z \times 10^4, y \times 10^5$) for carbon and oxygen atoms

Standard deviations are listed in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	7099 (2)	13193 (6)	−1185 (2)
C(2)	6575 (2)	13110 (8)	−2529 (2)
C(3)	5948 (2)	17402 (8)	−2995 (2)
C(4)	6029 (2)	20530 (7)	−1985 (2)
C(4a)	4961 (2)	18106 (6)	−1624 (1)
C(5)	4884 (2)	20715 (6)	−602 (2)
C(5a)	5342 (2)	17305 (5)	472 (1)
C(6)	4040 (2)	15560 (5)	617 (1)
C(6a)	4739 (2)	12780 (5)	1848 (1)
C(6b)	3712 (2)	11416 (5)	2341 (1)
C(7)	4410 (2)	12317 (6)	3743 (1)
C(8)	5913 (2)	9915 (7)	4383 (2)
C(9)	5726 (2)	5078 (7)	4282 (2)
C(10)	4091 (2)	4076 (6)	3578 (2)
C(10a)	3472 (2)	5770 (5)	2232 (1)
C(11)	4352 (2)	3779 (6)	1695 (2)
C(11a)	5239 (2)	7856 (5)	1542 (1)
C(12)	4868 (2)	8514 (5)	219 (1)
C(12a)	5894 (2)	12438 (5)	180 (1)
C(12b)	5667 (2)	12998 (6)	−1112 (1)
C(13)	7535 (2)	18676 (7)	−940 (2)
C(14)	3411 (2)	11404 (5)	−336 (1)
C(15)	3573 (2)	8406 (6)	4049 (1)
C(16)	8987 (2)	24114 (6)	810 (2)
C(17)	8488 (3)	28670 (8)	12 (2)
C(18)	10495 (2)	22356 (10)	1086 (2)
C(19)	9000 (2)	25117 (8)	1985 (2)
C(20)	1158 (2)	6455 (7)	−1459 (2)
C(21)	208 (2)	10290 (9)	−2405 (2)
C(22)	1905 (2)	3061 (8)	−1933 (2)
C(23)	233 (2)	3434 (9)	−1095 (2)
C(24)	1310 (2)	10405 (7)	4039 (2)
C(25)	1903 (3)	15397 (10)	4628 (3)
C(26)	1485 (3)	6489 (13)	4950 (3)
C(27)	−305 (2)	10814 (8)	3044 (2)
O(5)	4459 (2)	24902 (4)	−663 (1)
O(11)	4374 (2)	−521 (4)	1441 (1)
O(13)	7909 (1)	20176 (4)	248 (1)
O(14)	2232 (1)	8881 (4)	−334 (1)
O(15)	2017 (1)	8840 (5)	3394 (1)

amplitude was assigned an experimental weight based on a weighting scheme that has been described previously (Ealick & van der Helm, 1975a).

Structure determination and refinement

The structure was determined using direct methods and the program *MULTAN* (Germain, Main & Woolfson,

Table 3. *Positional parameters and isotropic temperature factors* (\AA^2) *for hydrogen atoms* ($x, z \times 10^3, y \times 10^4$)

Standard deviations are given in parentheses. Each hydrogen atom is assigned the number of the carbon atom to which it is attached.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	786 (2)	1079 (6)	-62 (2)	4.3 (4)
H(2)	665 (2)	1009 (7)	-296 (2)	6.2 (5)
H(3)	548 (2)	1867 (7)	-381 (2)	5.7 (5)
H(4)	582 (2)	2417 (6)	-215 (2)	4.3 (4)
H(4a)	391 (2)	1799 (6)	-233 (2)	4.0 (4)
H(5a)	613 (2)	1900 (6)	125 (1)	3.9 (4)
H(6)	334 (2)	1819 (6)	53 (1)	3.7 (4)
H(6a)	563 (2)	1469 (5)	251 (1)	3.0 (3)
H(6b)	276 (2)	1326 (6)	191 (1)	2.9 (3)
H(7)	439 (2)	1589 (6)	394 (2)	4.4 (4)
H(8)	684 (2)	1164 (7)	474 (2)	5.5 (5)
H(9)	653 (2)	280 (7)	457 (2)	5.3 (5)
H(10)	375 (2)	72 (7)	363 (2)	4.9 (4)
H(10a)	241 (2)	493 (6)	171 (1)	3.4 (4)
H(11a)	629 (2)	715 (5)	212 (1)	2.8 (3)
H(12)	486 (2)	547 (6)	-19 (1)	3.2 (3)
H(12a)	695 (2)	1173 (6)	76 (1)	3.1 (3)
H(12b)	504 (2)	1036 (6)	-163 (1)	3.5 (4)
H(13)	837 (2)	1953 (6)	-110 (1)	3.7 (4)
H(14)	308 (2)	1268 (5)	-118 (1)	2.2 (3)
H(15)	400 (2)	818 (6)	499 (2)	3.6 (4)
H(17A)	849 (2)	2822 (8)	-74 (2)	7.0 (6)
H(17B)	744 (3)	2958 (9)	-23 (2)	9.0 (7)
H(17C)	916 (2)	3142 (8)	43 (2)	7.7 (6)
H(18A)	1126 (2)	2483 (8)	162 (2)	7.8 (6)
H(18B)	1073 (3)	1901 (9)	154 (2)	9.0 (7)
H(18C)	1055 (2)	2178 (8)	36 (2)	7.2 (6)
H(19A)	799 (2)	2622 (8)	181 (2)	7.2 (6)
H(19B)	962 (2)	2203 (8)	252 (2)	6.8 (6)
H(19C)	979 (2)	2758 (7)	247 (2)	6.5 (5)
H(21A)	86 (3)	1230 (9)	-264 (2)	7.6 (6)
H(21B)	-56 (2)	866 (8)	-308 (2)	8.0 (7)
H(21C)	-21 (2)	1270 (8)	-202 (2)	7.0 (6)
H(22A)	112 (2)	150 (8)	-265 (2)	6.9 (6)
H(22B)	254 (2)	512 (7)	-217 (2)	6.4 (5)
H(22C)	253 (2)	44 (8)	-127 (2)	6.5 (5)
H(23A)	-9 (2)	546 (8)	-68 (2)	7.5 (6)
H(23B)	97 (2)	82 (8)	-40 (2)	7.0 (6)
H(23C)	-65 (2)	180 (7)	-188 (2)	6.1 (5)
H(25A)	298 (2)	1502 (8)	529 (2)	6.7 (5)
H(25B)	137 (3)	1636 (10)	502 (2)	10.3 (8)
H(25C)	177 (3)	1780 (11)	404 (3)	12.0 (9)
H(26A)	81 (3)	678 (11)	520 (3)	12.2 (9)
H(26B)	250 (3)	693 (8)	564 (2)	7.8 (6)
H(26C)	121 (3)	312 (11)	443 (3)	12.1 (9)
H(27A)	-70 (2)	753 (8)	261 (2)	6.9 (6)
H(27B)	-44 (2)	1348 (8)	241 (2)	7.0 (6)
H(27C)	-94 (3)	1165 (9)	343 (2)	9.0 (7)

1971). All C and O atoms were located in an *E* map calculated from the 495 *E* values greater than 1.67 and the signs from the *MULTAN* phase set showing the highest absolute figure of merit and lowest residual. The structure was refined using block-diagonal least-squares methods (Ahmed, 1966) in which the quantity $\sum w_F(kF_o - F_c)^2$ was minimized. The H atoms were located from a difference Fourier map based on the partially refined C and O atom positions. Least-squares refinement using isotropic temperature factors for H atoms and anisotropic temperature factors for C and O atoms was terminated when all shifts were less than the corresponding estimated standard deviations. The *R* value ($= \sum |kF_o - F_c| / \sum |kF_o|$) based on final parameters (Tables 2 and 3) is 0.068 for all 6520 data.

Atomic scattering factors for C and O atoms were taken from *International Tables for X-ray Crystallography* (1962), and those for H atoms from Stewart, Davidson & Simpson (1965). A final difference Fourier map showed no peaks larger than 0.2 e \AA^{-3} . In the structure factor analysis the value of $w_F(\Delta F)^2$ did not show a significant variation with either $|F_o|$ or $\sin^2 \theta$ thus validating the weighting scheme which was used.*

Results and discussion of the structure

The reaction of 7-*tert*-butoxynorbornadiene produces at least the following five products: (1) a cage dimer, (2) a dimer ketone, (3) a cyclic trimer monoketone, (4) a linear trimer diketone and (5) a telomer (Marchand & Hayes, 1977). The structures of the cage dimer (Neely, van der Helm, Marchand & Hayes, 1976), the dimer ketone (Ealick & van der Helm, 1975b) and the linear trimer diketone (this work) have been determined by single-crystal X-ray diffraction. The structure of the trimer diketone consists of the condensate of three 7-*tert*-butoxynorbornadiene residues alternating with two carbonyl groups which generate two cyclopentane rings. Each of the cyclopentanone rings results *via* iron pentacarbonyl-promoted coupling of a strained, olefinic double bond to carbon monoxide. The number of possible stereoisomers is large as a result of the following possibilities which are illustrated in Fig. 1: (1) each 7-*tert*-butoxynorbornadiene residue can couple *endo* or *exo*; (2) each *tert*-butoxy group can be *syn* or *anti* with respect to a given cyclopentanone ring; (3) the attachment to the cyclopentanone rings can be either *cis* or *trans*; (4) the attachment of the central 7-*tert*-butoxynorbornane entity may be *exo, exo*; *exo, endo*; or *endo, endo*; (5) the carbonyl groups of the two cyclopentanone rings can be either periplanar (pointed in the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33688 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

same direction) or antiperiplanar. The total number of stereoisomers possible for the structure is then 2304 (Hayes, 1975). The fact that only one enantiomeric pair of these isomers is observed indicates the remarkable stereospecificity of the coupling mechanism which is discussed elsewhere (Hayes, 1975; Marchand & Hayes, 1977). The molecule as viewed in the stereo-diagram (Fig. 2) can then be described going from right to left as the *syn-endo-trans-exo-syn-exo-antiperiplanar-trans-exo-syn* isomer. It is interesting to note that the left two-thirds of the molecule has a stereochemistry identical to that observed for the dimer ketone (Ealick & van der Helm, 1975*b*) thus suggesting

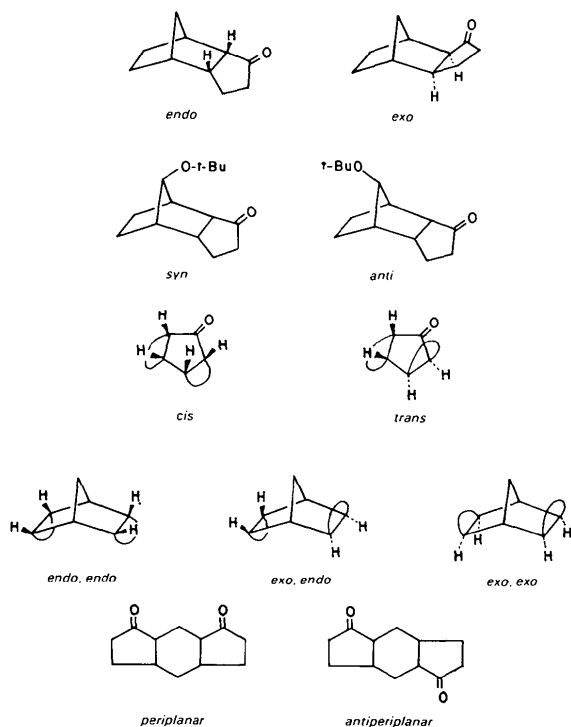


Fig. 1. Possible stereochemical configurations for trimer diketone subunits. Note: The use of *syn* and *anti* for the *R* group is with respect to the five-membered ring (Hayes, 1975; Marchand & Hayes, 1977).

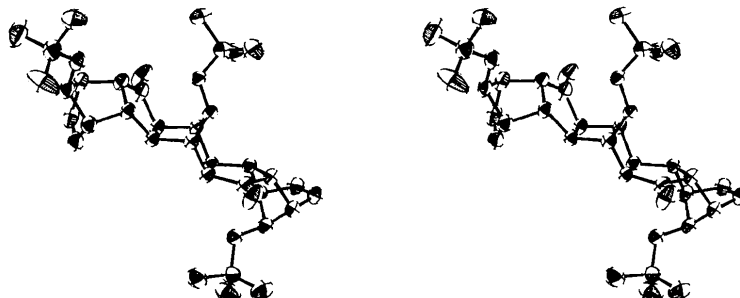


Fig. 2. Stereoview of a single molecule (Johnson, 1965).

that the trimer diketone is formed by stereospecific coupling of C≡O and an additional 7-*tert*-butoxy-norbornadiene molecule to one of the two double bonds in an intact dimer ketone. All *tert*-butoxy

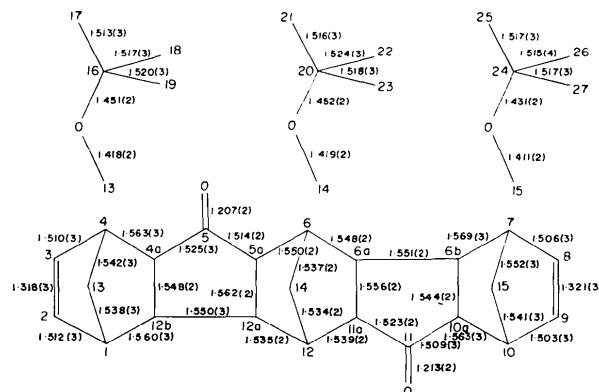


Fig. 3. Bond distances for the trimer diketone. The *tert*-butoxy groups have been detached for clarity.

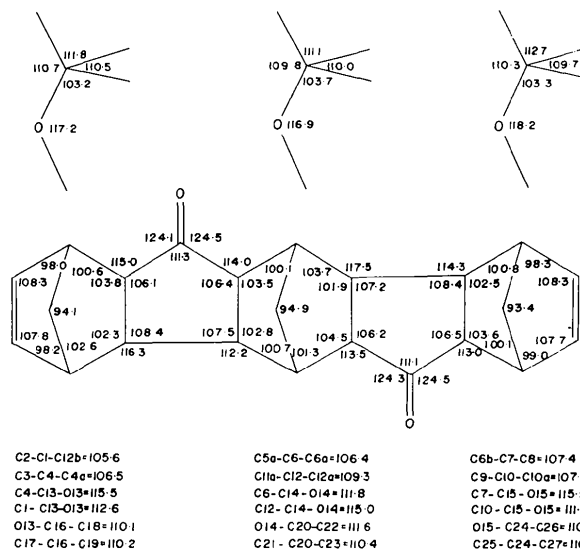
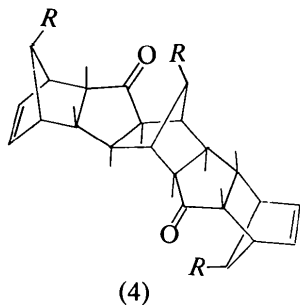


Fig. 4. Bond angles for the trimer diketone. The *tert*-butoxy groups have been detached for clarity. Estimated standard deviations are between 0.1 and 0.2°.

groups are nearly staggered in their attachment to the 7 position of the norbornane residue. The two cyclopentanone rings are essentially flat.



Bond distances and the IUPAC numbering scheme for the trimer diketone, (4), are given in Fig. 3 and bond angles are given in Fig. 4. Some of the C—C single bonds are lengthened from the normal value of 1.54 Å which can be taken as an indication of the strain present in the structure. The most interesting feature is a systematic shortening of the C—O bond lengths involving the bridge atom (7 position) of the norbornane entities. This shortening can be explained in terms of a hybridization effect at the bridge atom. Because of the strain present in the norbornane structure the bridge angle is decreased from the normal tetrahedral value of

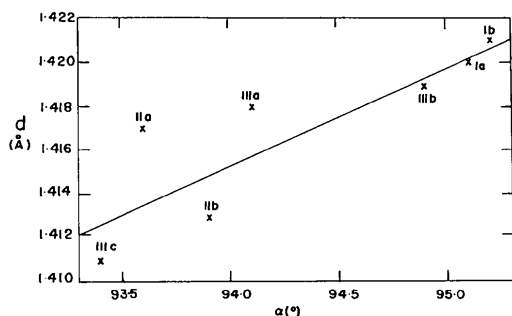


Fig. 5. Plot of the bridgehead carbon—oxygen distance versus bridge angle. Compounds are (I) cage dimer (Neely *et al.*, 1976), (II) dimer ketone (Ealick & van der Helm, 1975*b*) and (III) trimer diketone (this work).

109.5° to an average value of 94.1° in the trimer diketone. This results in an increase in the *p*-character of the molecular orbitals in the norbornane system and an increase in *s*-character in the exterior orbitals. This increased *s*-character in the exterior orbitals causes the observed shortening. It is unlikely that the effect is only an apparent shortening due to thermal motion as one would expect this to affect all C—O lengths, contrary to our observations. Such an effect is not unusual; similar observations have been made in such strained hydrocarbons as 1-biapocamphane, 1-binorbornane and 1-biadamantane (Alden, Kraut & Taylor, 1968).

As in the present study the effect observed by Alden *et al.* (1968) can be explained as a hybridization effect. Further evidence for a hybridization effect can be seen in ¹³C—H coupling constants for which the empirical relationship % *s*-character = $J_{13(C-H)}/500$ is well documented (Seebach, 1965). The value of 135.5 Hz has been reported for the $J_{13(C-H)}$ of the bridge H atom in norbornadiene and a value of 135 Hz for the same H atom in 2-benzonorbornane (Tori, Muneyuki & Tanida, 1963). This increase of 10 Hz over the value of 125 Hz expected for an *sp*³-hybridized atom indicated 27% *s*-character in these bonds and can explain the observed shortening if one assumes that the present molecule behaves in a similar manner. One must also be careful in making such comparisons because the electronegativity of the O atom and its effect on hybridization have been neglected.

Additionally, a corresponding effect was also observed in both the cage dimer (Neely *et al.*, 1976) and in the dimer ketone (Ealick & van der Helm, 1975*b*). If the C—O bond distance (d) is plotted against bridge angle (α) for the seven *tert*-butoxy groups in these three structures (Fig. 5) an approximate straight line is observed which is defined by the equation $d = 0.0042\alpha + 1.018$ where d is in Å and α is in degrees. The maximum deviation of any point from the line is 0.004 Å or about two standard deviations. By extrapolation one can calculate a value of 1.481 Å for $\alpha = 109.5^\circ$ which is close to a 'normal' C—O bond length in unstrained aliphatic ethers. Although the accuracy of this plot is limited by the fact that the points are highly

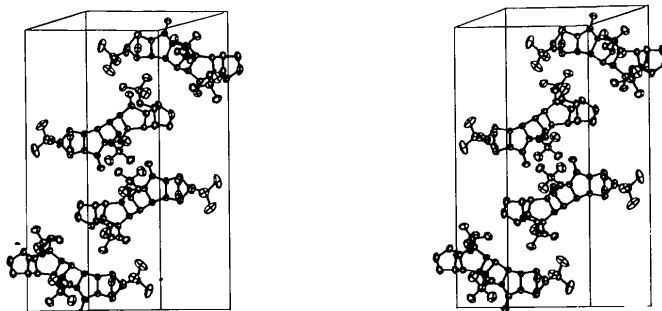


Fig. 6. Packing diagram for the trimer diketone (Johnson, 1965). The directions of the axes are *a* into the page, *b* ↑ *c* →.

clustered, the trend of a decreasing C—O bond length with decreasing bridge angle is clearly evident.

A packing diagram is shown in Fig. 6. In general the long direction of the molecules lies perpendicular to the *b* axis with the longest dimension of the molecules lying along the diagonal of the *ac* plane. No unusual intermolecular contacts were observed.

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The Crystal Structures of Mixed-Ligand Copper(II) Complexes.

I. Bis(3-aminopropyl)amine(di-2-pyridylamine)copper(II) Nitrate and Bis(3-aminopropyl)amine(2,2'-bipyridyl)copper(II) Nitrate

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The crystal structures of bis(3-aminopropyl)amine(di-2-pyridylamine)copper(II) nitrate, $C_{16}H_{26}N_8O_6Cu$ (I), and bis(3-aminopropyl)amine(2,2'-bipyridyl)copper(II) nitrate, $C_{16}H_{25}N_7O_6Cu$ (II), have been established by X-ray analysis. (I) is monoclinic, space group $P2_1/a$ with $a = 16.81$ (5), $b = 12.33$ (5), $c = 10.42$ (5) Å, $\beta = 99.5$ (5)°, $Z = 4$; and (II) is orthorhombic, space group $Pbca$ with $a = 13.96$ (5), $b = 13.02$ (5), $c = 22.58$ (8) Å, $Z = 8$. Both structures were solved by the heavy-atom method and refined to $R = 0.0707$ and 0.0739 for (I) and (II), respectively. Both structures are ionic lattices with the cations having a distorted five-coordinate square-pyramidal stereochemistry, but with significantly different angular distortions.

Introduction

A wealth of crystallographic data (Muetterties & Schunn, 1966; Hathaway & Billing, 1970) has established the existence of the five-coordinate square-based-pyramidal and trigonal-bipyramidal stereochemistries for the Cu^{II} ion, especially in mixed-ligand complexes. Due to the nature of the ligands present distorted geometries are involved, depending on the bite angles of the chelate ligands and the conformation of the polydentate chelate ligands (Gollogly & Hawkins, 1972). The present structures have been determined to demonstrate how the stereochemistry about the Cu^{II} ion varies with pairs of closely related ligands and ultimately to relate these to the detailed electronic properties of the Cu^{II} ion present.

Experimental

The complexes $Cu(bpa)(dpyam)(NO_3)_2$ (I)* and $Cu(bpa)(bpy)(NO_3)_2$ (II)* were prepared by mixing a hot solution of $Cu(NO_3)_2 \cdot 3H_2O$ in methanol (7 mmol in 5 ml) with an equimolar stoichiometric mixture of bis(3-aminopropyl)amine and di-2-pyridylamine (for I) and 2,2'-bipyridyl (for II) in methanol (7 mmol in 25 ml). Blue-black crystals of both (I) and (II) were formed on cooling; (I), found: C = 39.18, H = 5.30, N = 23.01; $C_{16}H_{26}N_8O_6Cu$ requires: C = 39.34, H = 5.12, N = 22.95%; and (II), found: C = 40.54, H = 5.28, N = 20.91; $C_{16}H_{25}N_7O_6Cu$ requires: C = 40.46, H = 5.30, N = 20.64%.

* Bis(3-aminopropyl)amine = bpa; di-2-pyridylamine = dpyam; 2,2'-bipyridyl = bpy.