Crystal Structure of *exo*-6-Chloromercurio-6,7-dihydro-*exo*-7-methoxyaldrin (1,2,3,4,10,10-Hexachloro-*exo*-6-chloromercurio-1,4,4a,5,6,7,8,8a-octahydro-*endo,exo*-1,4:5,8-dimethano-*exo*-7-methoxynaphthalene)

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Mercury(II) chloride and the chlorinated cyclodiene pesticide aldrin react in aqueous methanol to produce two mercury-containing products. The major product of this reaction involves the oxymercuration of the non-chlorinated double bond of aldrin. It has been identified as the *exo,cis* adduct in accord with the oxymercuration of other strained, bicyclic, olefinic systems. The crystal structure of the title adduct has been determined from single-crystal *X*-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 8.153(4), b = 19.536(5), c = 12.132(5) Å, β = 107.20(3)°, and Z = 4. Least-squares refinement gives a final R of 0.058 for the 2 301 unique reflections. The mercury–carbon and –chlorine distances are 2.08(2) and 2.317(5) Å, respectively.

THE oxymercuration–demercuration reaction for olefinic systems presents a synthetic reaction of considerable utility.[1] For simple, unhindered, olefinic systems the reaction proceeds to yield *trans* addition of the mercury(II) salt to the double bond. Strained bicyclic systems, however, give almost exclusively *exo-cis* addition.[2] The reasons for this change in product are unclear but appear to involve both steric and electronic factors.[1] Kinetic studies with substituted olefins [3] show good correlation between the rate constant and the Taft σ* parameter. The rate constant for the oxymercuration of propene decreases by a factor of 10^4 when the olefin reactant is 3-chloropropene. Similarly, the diolefin 1,2,3,4,7,7-hexachloronorbornadiene does not undergo oxymercuration at either the chlorinated or non-chlorinated carbon–carbon double bond.[1c]

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian A-60A, EM-360, or EM-390 spectrometer using $CDCl_3$ as a solvent with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 457 or Pye–Unicam SP 1000 spectrophotometer.

Reaction of Aldrin with $HgCl_2$.—A methanol solution of aldrin (0.300 g, 0.822 mmol, in 54 cm³) was added to $HgCl_2$ (2.0 g, 7.4 mmol) in water (18 cm³). A white solid gradually precipitated and was filtered off. Following washes with methanol–water, methanol, and hexane, the insoluble product was dissolved in the minimum amount of chloroform and spotted on thick layer chromatographic plates (20 × 20 cm) of silica gel G. These plates were developed in a saturated chamber of chloroform. After development, strips of silica gel G coating were sprayed with a 0.5% alcoholic solution of *sym*-diphenylcarbazone. The zones of the silica gel layer containing each compound (R_F 0.68 and 0.22) were collected and washed with chloroform–acetone (1 : 1 v/v). The solutions were filtered and evaporated on a steam-bath. Each residue was washed with three portions (10 cm³) of methanol. The white crystals of the major product (R_F 0.68) were dissolved in chloroform (3 cm³). Addition of methanol (2 cm³) to the chloroform solution produced a slightly turbid solution which was allowed to stand at room temperature for 3 h. The colourless needle-shaped crystals which precipitated were collected and washed with hexane (5 cm³). By this procedure the minor product (R_F 0.22) was not obtained in sufficient quantity for study.

Infrared spectrum of major product in KBr: 1 605s (C=C), 1 100s (C–O–C), 1 466m (O–Me), 326s (Hg–Cl), and 510w cm⁻¹ (C–Hg). N.m.r. spectrum in $CDCl_3$: δ 1.5 (m, 2 H), 2.3—2.8 (m, 5 H), 3.3 (d, J 6—7 Hz, 1 H), and 3.4 p.p.m. (s, 3 H).

X-Ray Data Collection.—Single crystals of the major product (0.062 × 0.20 × 0.50 mm) were sealed in thin-walled glass capillaries. Final lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections accurately centred on an Enraf–Nonius CAD-4 diffractometer.

Crystal data. $C_{13}H_{11}Cl_7HgO$, $M = 631.99$, Monoclinic, $a = 8.153(4)$, $b = 19.536(5)$, $c = 12.132(5)$ Å, $\beta = 107.20(3)°$, $U = 1\,845.8$ Å³, $D_c = 2.27$ g cm⁻³, $Z = 4$, $F(000) = 1\,184$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 95.08$ cm⁻¹.

Data were collected at 24 ± 1 °C on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique with a take-off angle of 3.5°. The

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[1] (*a*) W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61; (*b*) D. J. Pasto and J. A. Gontary, *J. Amer. Chem. Soc.*, 1971, **93**, 6902; (*c*) T. G. Traylor, *Accounts Chem. Res.*, 19C9, **2**, 152; (*d*) S. J. Cristol, J. S. Perry, and R. S. Beckley, *J. Org. Chem.*, 1976, **41**, 1912.

[2] T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 2746.

[3] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, 1967, **89**, 6427.

scan rate was variable and was determined by a fast 20° min^{-1} pre-scan. Calculated speeds for the slow scan (based on the net intensity gathered in the pre-scan) ranged from 7 to 0.4° min^{-1}. Other diffractometer parameters and the method of estimation of standard deviations have been described previously.[4] As a check on the stability of the instrument and crystal, three reflections were measured after every 30 reflections; no significant variation was noted.

One independent quadrant of data was measured out to 2θ 50°; a slow scan was performed on a total of 2 301 unique reflections. Since these data were scanned at a speed which would yield a net count of 4 000 the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 30 was obtained in the pre-scan. Based on these considerations, the data set of 2 301 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects [5] (the minimum and maximum transmission factors being 0.16 and 0.57, respectively).

TABLE 1

Final fractional co-ordinates for *exo*-6-chloromercurio-6,7-dihydro-*exo*-7-methoxyaldrin

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Hg	−0.029 59(10)	0.560 39(4)	0.349 87(6)
Cl(1)	−0.246 5(7)	0.511 6(4)	0.411 2(4)
Cl(2)	0.248 3(8)	0.810 2(2)	0.106 8(4)
Cl(3)	0.041 3(7)	0.718 6(3)	−0.120 2(4)
Cl(4)	0.294 1(8)	0.585 3(2)	0.148 8(3)
Cl(5)	0.660 7(7)	0.595 0(3)	0.058 1(4)
Cl(6)	0.571 8(7)	0.764 9(3)	−0.003 8(4)
Cl(7)	0.649 4(7)	0.733 1(3)	0.234 4(4)
O	0.181 7(17)	0.475 4(6)	0.278 8(10)
C(1)	0.173 3(21)	0.600 5(9)	0.298 5(12)
C(2)	0.124 8(22)	0.640 2(8)	0.180 7(13)
C(3)	0.295 9(22)	0.674 5(8)	0.185 9(11)
C(4)	0.312 1(22)	0.727 7(8)	0.087 9(12)
C(5)	0.235 1(21)	0.694 3(8)	−0.029 0(12)
C(6)	0.329 6(22)	0.644 4(8)	−0.041 5(11)
C(7)	0.478 2(21)	0.639 2(8)	0.068 5(12)
C(8)	0.409 2(21)	0.614 4(8)	0.169 7(11)
C(9)	0.290 4(21)	0.551 7(7)	0.152 8(12)
C(10)	0.278 8(21)	0.537 2(8)	0.278 1(15)
C(11)	0.500 2(23)	0.716 4(9)	0.099 2(12)
C(12)	0.105 0(23)	0.579 7(8)	0.095 4(13)
C(13)	0.283 4(34)	0.416 1(9)	0.292 6(20)
H(1) [C(1)]	0.234 *	0.634	0.360
H(2) [C(2)]	0.023	0.673	0.163
H(3) [C(3)]	0.325	0.702	0.259
H(4) [C(8)]	0.514	0.601	0.234
H(5) [C(9)]	0.327	0.513	0.109
H(6) [C(10)]	0.394	0.532	0.338
H(7) [C(12)]	0.011	0.546	0.099
H(8) [C(12)]	0.082	0.594	0.013

* Hydrogen atoms were placed in calculated positions (1.00 Å from the bonded carbon atom) with *B* 5.0 Å^2.

The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral-atom scattering factors were taken from the compilations of Cromer and Waber [6] for Hg, Cl, O, and C; those for H were from ref. 7. The scattering by Hg was corrected for the real and imaginary components of anomalous dispersion using data from ref. 8.

Solution and Refinement of Structure.—The mercury atom was readily located on a Patterson map, and a difference-Fourier synthesis phased on the mercury-atom position afforded the co-ordinates of the remaining non-hydrogen atoms. Least-squares refinement with isotropic temperature factors gave *R* 0.12. Conversion into anisotropic thermal parameters and further refinement yielded *R* 0.065. The placement of the eight geometry-fixed hydrogen atoms in calculated positions and more cycles of least-squares refinement led to final values of *R* 0.058 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.063$. The co-ordinates of the three methyl hydrogen atoms were not determined. The weighting scheme was based on essentially unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The estimated standard deviation of an observation of unit weight was 1.33. Final values of the positional parameters are given in Table 1; observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22305 (12 pp.).*

TABLE 2

Bond distances (Å) and angles (°)

(*a*) Distances			
Hg–Cl(1)	2.317(5)	Hg–Cl(1)	2.08(2)
C(4)–Cl(2)	1.73(2)	C(5)–Cl(3)	1.71(2)
C(6)–Cl(4)	1.70(1)	C(7)–Cl(5)	1.76(2)
C(11)–Cl(6)	1.80(2)	C(11)–Cl(7)	1.76(1)
O–C(10)	1.45(2)	O–C(13)	1.41(2)
C(1)–C(2)	1.58(2)	C(1)–C(10)	1.57(2)
C(2)–C(3)	1.53(2)	C(2)–C(12)	1.55(2)
C(3)–C(4)	1.62(2)	C(3)–C(8)	1.54(2)
C(4)–C(5)	1.52(2)	C(4)–C(11)	1.51(2)
C(5)–C(6)	1.28(2)	C(6)–C(7)	1.52(2)
C(7)–C(8)	1.51(2)	C(7)–C(11)	1.55(2)
C(8)–C(9)	1.54(2)	C(9)–C(10)	1.58(2)
C(9)–C(12)	1.57(2)		
(*b*) Angles			
Cl(1)–Hg–C(1)	177.3(5)	C(10)–O–C(13)	113(1)
Hg–C(1)–C(2)	117(1)	Hg–C(1)–C(10)	106(1)
O–C(10)–C(1)	109(1)	O–C(10)–C(9)	110(1)
Cl(2)–C(4)–C(3)	114(1)	C(2)–C(4)–C(5)	118(1)
Cl(2)–C(4)–C(11)	117(1)	C(3)–C(5)–C(4)	122(1)
Cl(3)–C(5)–C(6)	128(1)	C(4)–C(6)–C(5)	130(1)
Cl(4)–C(6)–C(7)	123(1)	C(5)–C(7)–C(6)	116(1)
Cl(5)–C(7)–C(8)	114(1)	C(5)–C(7)–C(11)	117(1)
Cl(6)–C(11)–Cl(7)	106.0(8)	C(6)–C(11)–C(4)	113(1)
C(6)–C(11)–C(7)	113(1)	C(7)–C(11)–C(4)	117(1)
C(7)–C(11)–C(7)	114(1)	C(2)–C(1)–C(10)	104(1)
C(1)–C(2)–C(3)	101(1)	C(1)–C(2)–C(12)	100(1)
C(3)–C(2)–C(12)	106(1)	C(2)–C(3)–C(4)	121(1)
C(2)–C(3)–C(8)	103(1)	C(4)–C(3)–C(8)	102(1)
C(3)–C(4)–C(5)	108(1)	C(3)–C(4)–C(11)	98(1)
C(5)–C(4)–C(11)	99(1)	C(4)–C(5)–C(6)	110(1)
C(5)–C(6)–C(7)	107(1)	C(6)–C(7)–C(8)	109(1)
C(6)–C(7)–C(11)	99(1)	C(8)–C(7)–C(11)	99(1)
C(7)–C(8)–C(9)	120(1)	C(7)–C(8)–C(3)	103(1)
C(3)–C(8)–C(9)	104(1)	C(8)–C(9)–C(10)	103(1)
C(8)–C(9)–C(12)	105(1)	C(10)–C(9)–C(12)	100(1)
C(1)–C(10)–C(9)	102(1)	C(4)–C(11)–C(7)	94(1)
C(2)–C(12)–C(9)	94(1)		

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[4] J. L. Atwood and K. D. Smith, *J. Amer. Chem. Soc.*, 1973, **95**, 1488.

[5] D. J. Wehe, W. R. Busing, and H. A. Levy, 'ORABS, A Fortran Program for Calculating Single Crystal Absorption Corrections,' Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3, p. 202.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

RESULTS AND DISCUSSION

The reaction of aldrin with mercury(II) chloride leads to the formation of two stable mercury-containing products that can be readily separated and isolated using common chromatographic techniques.[9] The major product has been shown to be the *exo,cis* adduct of aldrin. Preliminary work indicates that the minor product is the corresponding *exo*-6-chloromercurio-*exo*-hydroxy-adduct of aldrin.[10] The chlorinated double bond of aldrin is not involved in the reaction. These results are in accord with literature observations cited earlier.[1-3]

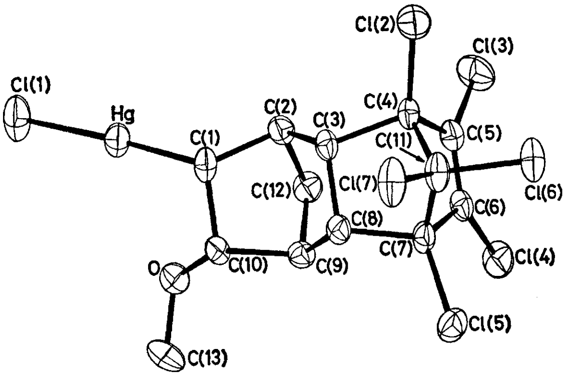

FIGURE 1 Molecular structure and atom-numbering scheme for the mercury adduct with the atoms displayed as 40% probability ellipsoids for thermal motion. Hydrogen atoms are not shown.

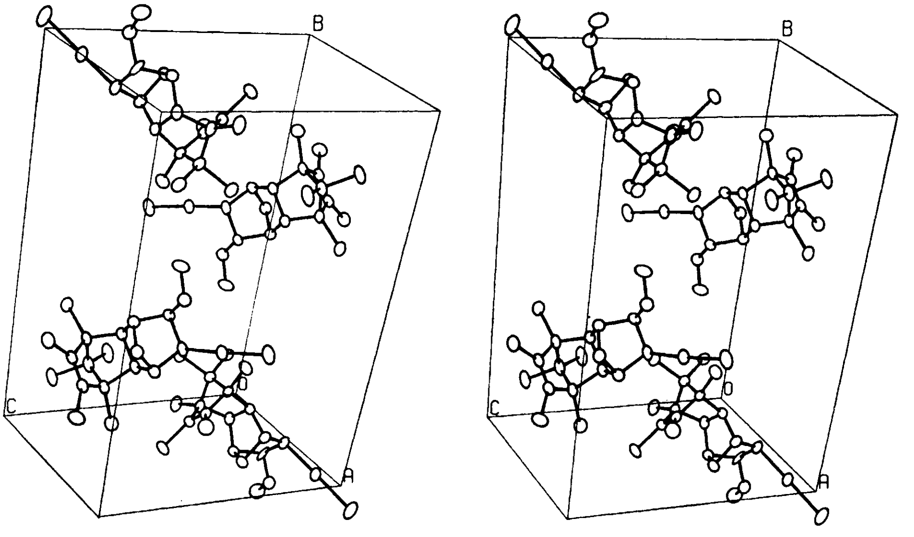

FIGURE 2 Stereoscopic view of the unit-cell packing in the mercury adduct

The molecular structure and atom-numbering scheme for the *exo,cis* adduct are shown in Figure 1, while the important bond distances and angles are given in Table 2. Figure 2 contains a stereoscopic view of the unit-cell packing. The oxymercuration of the non-chlorinated double bond does not appear to result in any stereochemical change in the aldrin system.[11] In fact, a comparison of the *exo,cis* adduct with the parent aldrin (Table 3) shows that the only significant structural change is that associated with the previously mentioned double bond. Many of the single bonds are slightly elongated because of ring strain, but the double bond [1.28(2) Å] is close to the accepted[12] value (1.335 Å). The average of the carbon(sp^3)–chlorine bond lengths [1.74(3) Å] agrees well with the accepted[13] value [1.767(5) Å].

TABLE 3

Comparison of bond distances (Å) for the carbon-atom framework of aldrin and *exo*-6-chloromercurio-6,7-dihydro-*exo*-7-methoxyaldrin

Bond[a]	Aldrin[b]	Mercury adduct
C(1)–C(2)	1.52	1.58
C(1)–C(10)	1.33	1.57
C(2)–C(3)	1.56	1.53
C(2)–C(12)	1.55	1.55
C(3)–C(4)	1.55	1.62
C(3)–C(8)	1.56	1.54
C(4)–C(5)	1.50	1.52
C(4)–C(11)	1.54	1.51
C(5)–C(6)	1.31	1.28
C(6)–C(7)	1.51	1.52
C(7)–C(8)	1.57	1.51
C(7)–C(11)	1.55	1.55
C(8)–C(9)	1.55	1.54
C(9)–C(10)	1.54	1.58
C(9)–C(12)	1.53	1.57
C(4)–Cl(2)	1.748	1.73
C(5)–Cl(3)	1.703	1.71
C(6)–Cl(4)	1.706	1.70
C(7)–Cl(5)	1.753	1.76
C(11)–Cl(6)	1.784	1.80
C(11)–Cl(7)	1.765	1.76

[a] Standard deviations in the distances are 0.01 Å for aldrin and 0.02 Å for the adduct. [b] Ref. 11.

Mercury–chlorine and –carbon bond lengths are given

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[9] Aldrich N. K. Lau, M.S. Thesis, Tuskegee Institute, 1975.

[10] Nirupam Trivedi, M.S. Thesis, Tuskegee Institute, 1978.

[11] T. P. DeLacy and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2153.

[12] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, 1960, **32**, 824.

[13] L. E. Sutton, 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' *Special Publ.*, The Chemical Society, London, 1965, no. 18.

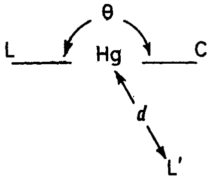
in Table 4. The Hg–Cl length in the present study (2.317 Å) is seen as typical for that of a two-co-ordinate mercury atom. A normal value of an Hg–C bond length is not so easily deduced. For the distances given in Table 4, a correction for hybridization is of little benefit because of two primary difficulties, one electronic and one experimental. First, the mercury–carbon bond is undoubtedly sensitive to additional ' weak ' interactions in which the mercury atom may participate. Thus, as shown below, for a two-co-ordinate mercury atom (bonded to a carbon atom and another ligand, L) there may be other forces brought to bear by other ligands, L′. If the distance *d* is ' short ' (a bonded distance) or ' long ' (greater than the sum of the van der Waals radii) then the interpretation is clear; otherwise it is not. A secondary manifestation of this effect may be a deviation of θ from 180°. For all the compounds given in Table 4, θ was close to 180°, but the implications for the bonding are not straightforward. The second difficulty associated with the mercury–carbon lengths is just that a carbon atom, especially a methyl-carbon atom, does not always refine well in the presence of the heavy atom. Some evidence of this problem is seen in the high estimated standard deviations associated with these lengths.

TABLE 4

Comparison of mercury–carbon and –chlorine bond distances (Å) [a]

Compound	Hg–C	Hg–Cl	Ref.
[HgMe{$O_2CCH(NH_3)CMe_2S$}]	1.82(5) 1.98(6)		*b*
[MeHg{$SCMe_2CH(CO_2)NH_2$}HgMe]	1.885(7) 2.165(6)		*c*
Hg($C_{13}H_{11}Cl_7O$)	2.08(2)	2.317(5)	This study
$HgMe_2$	2.083(5)		
[Hg(CCl_3)Cl]·$C_{12}H_8N_2$	2.10	2.31	*d*
[Hg(CH_2Ph)($SCPh_2$)]	2.10		*e*
Hg($C_{19}H_{21}N_2O$)$_2$	2.109(4)		*f*
[Hg{CH($COBu^t$)$_2$}(O_2CMe)]	2.11(2)		*g*
[Hg($CH_2CH_2Et_2$)Cl]	2.13(3)	2.36(1)	*h*
[HgMe(N_3)]	2.27(11)		*i*
$HgCl_2$		2.252(5)	*j*

[a] Only compounds in which the mercury atom is essentially two-co-ordinate are included. [b] Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1973, 741. [c] Y. S. Wong, P. C. Chieh, and A. J. Carty, *Canad. J. Chem.*, 1973, **51**, 2597. [d] A. D. Redhouse, *J.C.S. Chem. Comm.*, 1972, 1119. [e] R. D. Bach, A. T. Weibel, W. Schmonsees, and M. D. Glick, *J.C.S. Chem. Comm.*, 1974, 961. [f] H. Sawai, T. Takizawa, and Y. Iitaka, *J. Organometallic Chem.*, 1976, **120**, 161. [g] R. Allmann and H. Musso, *Chem. Ber.*, 1973, **106**, 3001. [h] K. Toman and G. G. Hess, *J. Organometallic Chem.*, 1973, **49**, 133. [i] U. Müller, *Z. Naturforsch.*, 1973, **286**, 426. [j] K. Kashiwabara, S. Konaka, and M. Kimura, *Bull. Chem. Soc. Japan*, 1973, **46**, 410.



With both factors considered, the value of the mercury–carbon distance found in the present study (2.08 Å) is probably very close to the standard. It also agrees nicely with the distance found [2.083(5) Å] by electron diffraction for $HgMe_2$.[14]

The molecular packing (Figure 2) does not present any abnormally close contacts. This is also borne out by the Cl(1)–Hg–C(1) angle (θ) of 177.3(5)°.

[7/2176 *Received*, 13*th December*, 1977]

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[14] K. Kashiwabara, S. Konaka, T. Iijima, and M. Kimura, *Bull. Chem. Soc. Japan*, 1973, **46**, 407.