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Three-Dimensional Linkage by Electron Donor–Acceptor Interactions: Complexes of Organic Ammonium Halides with Triiodomethane

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The preparation of a series of crystalline organylammonium halide complexes with triiodomethane is reported. The crystal structures of three complexes have been determined from single-crystal X-ray diffractometry data. The characteristic crystal data of the complexes are compared and their structures are discussed. The $I^-\cdots I$ distances are about 0.75 Å shorter than that anticipated for van der Waals contact, indicating that electron donor–acceptor bonds are present. The $I^-\cdots I$–C arrangement is nearly linear in all cases. Three-dimensional space networks as well as smaller units are formed by I^- anions and triiodomethane molecules due to charge-transfer interactions. Raman data of a few of the charge-transfer complexes are quoted. Several bands are shifted from their positions in the pure components and some degenerate modes are split. Electrical conductivity measurements show some of the complexes are organic semiconductors in the solid state. ^{13}C NMR investigations in Me_2SO-d_6 verify the existence of a charge transfer from iodide ions to HCI_3 molecules also in the dissolved state. The complex formation constant (K = 2.0 L/mol, in Me_2SO-d_6) has been determined from the I^- concentration dependence of the chemical shift of the HCI_3 carbon nucleus.

Introduction

Organic oligo onium compounds are distinguished by their uncommon versatile inclusion ability. A characteristic feature of their clathrates is the absence of strong binding interactions between hosts and guests. Apparently, the guest molecules are fixed sterically by the stable ionic host lattice.[1-4] The crystallization of these clathrates usually occurs slowly from alcoholic solutions or requires the addition of inert solvents (diethyl ether). In contrast, we found that the formation of the triiodomethane adducts takes place easily. Most of the organylammonium iodides ("organyl" is alkyl and/or aryl) prepared (Figure 1) form solid complexes with HCI_3 within a few minutes, even if they do not include other guest molecules.

It is known that triiodomethane forms solid charge-transfer complexes with n-donors such as 1,4-dioxane, 1,4-dithiane, 1,4-diselenane, quinoline, and other neutral molecules.[5-8] In the 1,4-dithiane–HCI_3 complex, chains of alternating donor and acceptor molecules have been found by X-ray analysis.[6] From ^{127}I NQR measurements it has been suggested that sp^3d-hybridized iodine atoms are present.[9] IR and Raman spectra of the complexes have been examined.[10]

Less work has been done on complexes between halides and triiodomethane. Several adducts of organic onium salts with HCI_3 had been reported in 1928, but without clarification of the complexs' nature.[11] Another investigation has shown by IR and ^1H NMR data that the anions of tetraalkylammonium halides associate specifically with trihalomethanes in weakly solvating media. It was presumed that especially triiodomethane bonds via the iodine atoms with halogen anions by means of charge-transfer interactions.[12]

Therefore the question was, whether the triiodomethane adducts had to be considered as clathrates or as complexes of the charge-transfer type. For this reason, we have synthesized a series of new organylammonium salt complexes with triiodomethane and studied their nature in detail by X-ray analysis and other spectroscopic methods.

Experimental Section

Oligo Ammonium Salts. Figure 1 shows the prepared organylammonium salts tested on complex formation with triiodomethane.

The salts **1–5** were synthesized by aminomethylation of azulene and subsequent addition of alkyl halide. The triiodide **4** is formed in the reaction of compound **1** with a stoichiometric amount of iodine in methanol. The salts **6–15**, **17**, **18**, **21**, and **23–25** were obtained starting from the corresponding benzyl bromides or chlorides by reaction with dialkylamine in a sealed tube and followed by alkylation. Salt **16** was prepared from 1,3-phenylenebis(acetonitrile) by reduction with $LiAlH_4$ and permethylation. The ammonium compounds **19**, **20**, and **22** were obtained by methylation of the corresponding amines with iodomethane.[4]

Triiodomethane Complexes. On addition of a nearly saturated solution of triiodomethane in methanol or ethanol to a solution of the ammonium salt in the same solvent, the adducts precipitated mostly quantitatively within a few minutes. The greater part of the ammonium salts forms adducts with HCI_3 in different ratios (Table I). No complexes have been obtained with the salts **3**, **7**, **9–12**, **15**, **22**, and **23** until now.

X-ray Analyses. Crystals of complexes **4**·2 HCI_3 and **8**·2 HCI_3 and **19**·HCI_3 were grown from ethanol and methanol, respectively, by slow cooling. The crystal data are listed in Table II.

Structure Determinations. The intensity data were collected on a four-circle diffractometer CAD 4 (Enraf Nonius) using graphite-crystal monochromatized Mo K_α radiation. No absorption corrections were made.

The cell dimensions were obtained by least-squares refinement of the positions of 25 reflexions. The number of formula units, Z, were estimated from the approximate space requirements (I, 0.050 nm^3; C, N, 0.020 nm^3).

Systematic absences indicated that the space group of the complex **4**·2 HCI_3 is $P2_1/c$. The space groups of the complexes **8**·2 HCI_3 and **19**·HCI_3 could not be determined definitely from the systematic absences. Respectively two space groups were possible, Pc or $P2/c$ for **19**·HCI_3 and Cc or $C2/c$ for **8**·2 HCI_3. In

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[†] Institut für Organische Chemie and Biochemie.

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(1) Vögtle, F.; Löhr, H.-G.; Puff, H.; Schuh, W. *Angew. Chem.* **1983**, *95*, 425; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 409; *Angew. Chem. S.* **1983**, 527–536.

(2) Löhr, H.-G.; Vögtle, F.; Schuh, W.; Puff, H. *J. Chem. Soc., Chem. Commun.* **1983**, 924.

(3) Löhr, H.-G.; Vögtle, F.; Schuh, W.; Puff, H. *J. Incl. Phenom.* **1983**, *1*, 175–179.

(4) Löhr, H.-G.; Josel, H.-P.; Engel, A.; Vögtle, F.; Schuh, W.; Puff, H. *Chem. Ber.*, in press.

(5) Bjorvatten, T. *Acta Chem. Scand.* **1969**, *23*, 1109–1118.

(6) Bjorvatten, T.; Hassel, O. *Acta Chem. Scand.* **1961**, *15*, 1429–1436.

(7) Bjorvatten, T.; Hassel, O. *Acta Chem. Scand.* **1962**, *16*, 249–255.

(8) Bjorvatten, T. *Acta Chem. Scand.* **1963**, *17*, 2292.

(9) Okuda, T.; Ishihara, H.; Yamada, Y.; Negita, H. *Chem. Lett.* **1979**, 825–828.

(10) Hayward, G. C.; Hendra, P. J. *Spectrochim. Acta* **1967**, *23*, 1937–1943.

(11) Steinkopf, W.; Teichmann, H. *J. Prakt. Chem.* **1930**, *127*, 337–356.

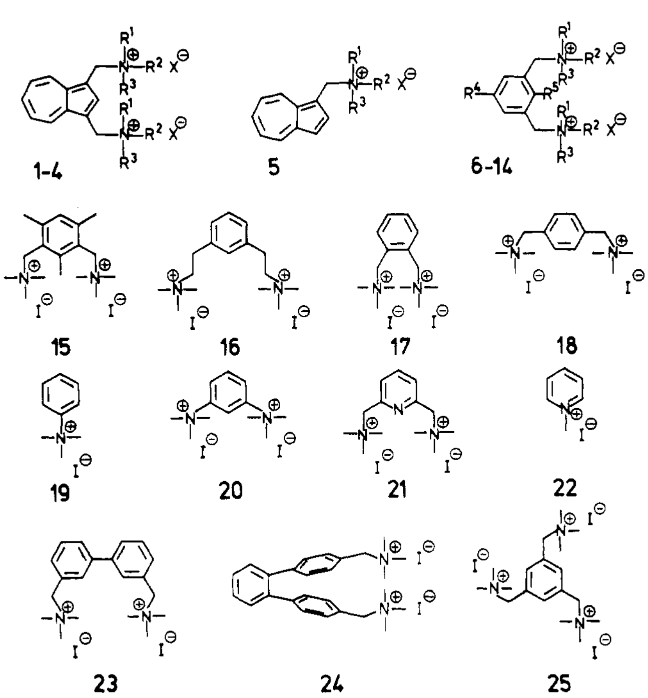
(12) Green, R. D.; Martin, J. S. *J. Am. Chem. Soc.* **1968**, *90*, 3569–3668.

0022-3263/84/1949-1621$01.50/0

Table I. Triiodomethane Complexes of Organyl Ammonium Halides

compd	ammonium halides	molar ratio of salt:triiodomethane[a]	ratio donor (I^-): acceptor (HCI_3)	mp or complex dec temp, °C
1	azulene-1,3-diylbis(methylenetrimethylammonium) diiodide	1:2	1:1	158-160 dec
2	azulene-1,3-diylbis(methylenetrimethylammonium) dibromide	1:2	1:1	153 dec
4	azulene-1,3-diylbis(methyleneethyldimethylammonium) diiodide	1:2	1:1	123-127
5	(azulene-1-ylmethyl)trimethylammonium iodide	1:1	1:1	180-183 dec
6	1,3-phenylenebis(methylenetrimethylammonium) diiodide	1:3	2:3	125-133
8	5-*tert*-butylphenylene-1,3-bis(methylenetrimethylammonium) diiodide	1:2	1:1	159-164
13	1,3-phenylenebis(methylenetriethylammonium) diiodide	1:2	1:1	153
14	1,3-phenylenebis(methylenetriethylammonium) dibromide	1:1	1:1	125-126
16	1,3-phenylenebis(ethylenetrimethylammonium) diiodide	1:2	1:1	123-126
17	1,2-phenylenebis(methylenetrimethylammonium) diiodide	1:2	1:1	180-183
18	1,4-phenylenebis(methylenetrimethylammonium) diiodide	1:4	1:2	122-123
19	phenyltrimethylammonium iodide	1:1	1:1	182-184
20	1,3-phenylenebis(trimethylammonium) diiodide	1:4	1:2	157-158
21	pyridine-1,3-diylbis(methylenetrimethylammonium) diiodide	1:2	1:1	121-125
24	*o*-terphenylene-4,4''-bis(methylenetrimethylammonium) diiodide	2:1	4:1	151-161
25	1,3,5-benzenetriyltris(methylenetrimethy ammonium) triiodide	1:2	3:2	156-159

[a] The molar ratios were determined by integration of the ^1H NMR spectra, employing Me_2SO-d_6 as solvent.



Nr.	R^1	R^2	R^3	R^4	R^5	X
1	CH_3	CH_3	CH_3	-	-	I
2	CH_3	CH_3	CH_3	-	-	Br
3	CH_3	CH_3	CH_3	-	-	I_3
4	C_2H_5	CH_3	CH_3	-	-	I
5	CH_3	CH_3	CH_3	-	-	I
6	CH_3	CH_3	CH_3	H	H	I
7	CH_3	CH_3	CH_3	CH_3	H	I
8	CH_3	CH_3	CH_3	t-Bu	H	I
9	CH_3	CH_3	CH_3	NO_2	H	I
10	CH_3	CH_3	CH_3	OCH_3	H	I
11	CH_3	CH_3	CH_3	H	OCH_3	I
12	CH_3	CH_3	CH_3	OCH_3	OCH_3	I
13	C_2H_5	C_2H_5	C_2H_5	H	H	I
14	C_2H_5	C_2H_5	C_2H_5	H	H	Br

Figure 1. Prepared organylammonium salts.

both cases the space groups were assumed as noncentrosymmetric due to the estimated number of formula units and the absence of two-fold axes and centers of symmetry in the expected molecular structures. Accordingly, the structures could only be solved in the space groups *Pc* ($19\cdot HCI_3$) and *Cc* ($8\cdot 2\ HCI_3$).

The positions of the iodine atoms were found by direct methods ($4\cdot 2\ HCI_3$,[13] $8\cdot 2\ HCI_3$,[14] $19\cdot HCI_3$[14]). The other atoms, except the hydrogens, were located in difference fourier maps. Anisotropic thermal parameters for the iodine atoms and isotropic (for $19\cdot HCI_3$ also anisotropic) thermal parameters for the carbon and nitrogen atoms were applied. The structures were refined by full-matrix least-squares methods[13] with unit weights for $4\cdot 2\ HCI_3$ and weights $w = [\sigma^2(F) + 0.002F^2]^{-1}$ for $19\cdot HCI_3$ and $8\cdot 2\ HCI_3$. The numbering system is shown in Figure 2.

Raman Spectra. The Raman spectra were recorded on a Laser-Raman spectrometer Coderg LRT 800. A crypton laser, operating at a wavelength of 647.1 nm, was used. Triiodomethane and the complexes were examined as solids.

Electrical Conductivity. The conductivities of three solid complexes were determined as compressed powders. The obtained values of the specific conductivities are: $8\cdot 2\ HCI\ 7.1 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$, $4\cdot 2\ HCI_3\ 2.5 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$, $19\cdot HCI_3\ 1.8 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$.

^{13}C NMR Spectra. The NMR spectra were obtained on a WH-90 spectrometer (Bruker Physik AG, Karlsruhe). Tetramethylsilane (Me_4Si) was used as internal reference. All measurements were carried out in hexadeuteriodimethyl sulfoxide (Me_2SO-d_6). Volumetric tubes (2 mL) were weighed before and after addition of phenyltrimethylammonium iodide and triiodomethane. Enough solvent (ca. 1 mL) was added to dissolve the solids. After adding 10 drops of Me_4Si the solutions were filled up to the mark with solvent, mixed, and transferred to the NMR tubes.

Complex Formation Constant. Assuming only the presence of 1:1 complexes of donor (iodide ions) and acceptor (triiodomethane), the eq 1b defines the equilibrium constant of the reaction 1a.

$$D + A \rightleftharpoons C \tag{1a}$$

$$K = \frac{[C]}{[D]\,[A]} \tag{1b}$$

Because of the high exchange rate, only one sharp carbon signal for HCI_3 is observed in the NMR spectra, monotonically shifted downfield with increasing iodide concentration (Figure 3). Scotts modification[15] (eq 2) of the Benesi-Hildebrand method[16] has been used to determine values of Δ_c and K (cf. ref 12).

$$\frac{[D]}{\Delta} = \frac{1}{K\Delta_c} + \frac{[D]}{\Delta_c} \tag{2}$$

with $\Delta = \sigma - \sigma_A$ the difference between the observed shielding

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[13] Sheldrick, G. M. SHELX-76: Program for Crystal Structure Determination, Cambridge, 1976.

[14] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. MULTAN 80: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, York, 1980.

[15] Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787.

[16] Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

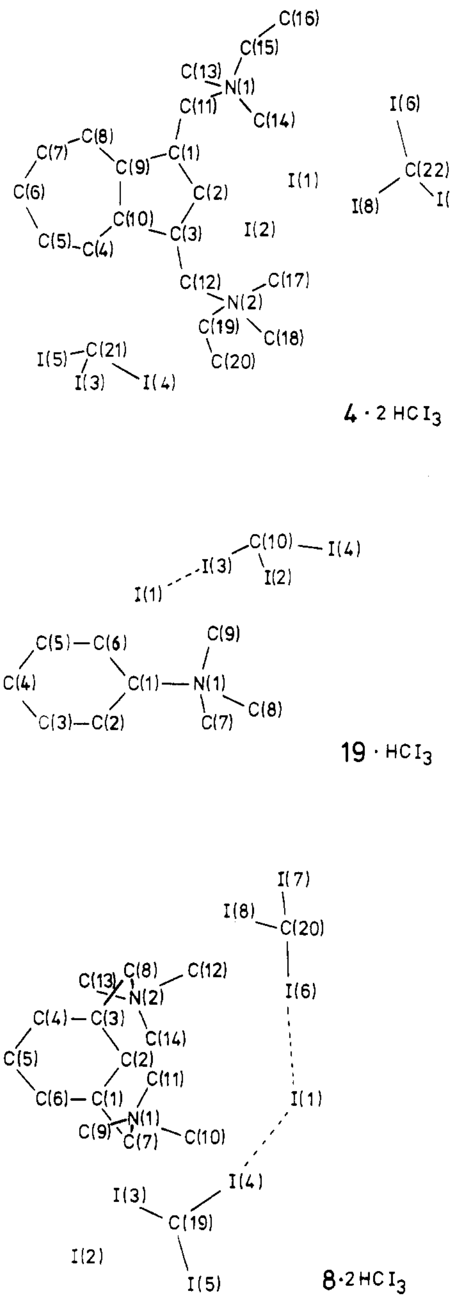

Figure 2. Numbering scheme of C, I, and N atoms in the complexes.

and the shielding in pure triiodomethane, and $\Delta_c = \sigma_c - \sigma_A$ the difference between the shielding in the pure complex and in pure triiodomethane; Δ_c cannot be observed directly. As the acceptor concentration had been kept small, the total initial salt concentration was approximately [D]. The plot of [D]/Δ against [D] is linear as required by eq 2. The values of Δ_c and K were calculated by using a least-squares analysis.

Results and Discussion

Structures of the Complexes. The X-ray structures of the three complexes 4·2 HCI_3, 8·2 HCI_3, and 19·HCI_3 indicate that the triiodomethane molecules are connected in all cases via iodine atoms with iodide ions. The presence of electron donor–acceptor bonds is indicated by the following items: (a) The shortest $I^- \cdots I$ distances are 3.47–3.69 Å; i.e., about 0.75 Å less than the sum of the van der Waals radii (4.35 Å). (b) The C–I distances in the complexes are slightly longer than in pure triiodomethane (2.11 Å[17]). (c) The $I^- \cdots I$–C arrangements are always nearly linear.[18] The characteristic data of the donor–acceptor bonds, and all intra- and intermolecular I···I distances below 4.35 Å, are listed in Table III.

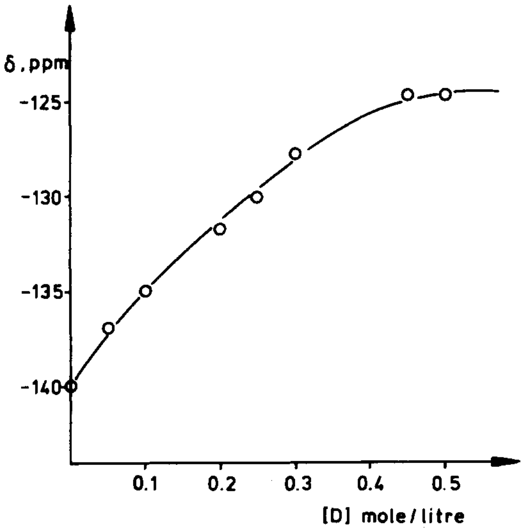

Figure 3. Carbon shielding (of 0.05 M HCI_3, in Me_2SO-d_6) vs. phenyltrimethylammonium iodide concentration.

The HCI_3 molecules in the complexes are strongly distorted. The I–C–I angles are on average (111.5°) smaller than in pure HCI_3 (114.6° [17]). Because the reduction of the I–C–I angles is found in all three X-ray analyses, it seems not to be an effect of the molecular packing. However, it might be caused by the intermolecular charge transfer from the iodine ion to the acceptor molecules. One possible explanation is based on the observed lengthening of the C–I bonds. On the supposition that an intermolecular $n \rightarrow \sigma^*$ transition takes place, the lengthening of the concerned C–I bond is conceivable. The average C–I length found in the complexes amounts to 2.16 Å. The deviation of the I–C–I angles in pure HCI_3 from the ideal tetrahedral arrangement is caused by the repulsion of the iodine atoms. The C–I bond lengthening in the complexes allow a diminishing of the I–C–I angles *without* concomitant approach of the iodine atoms; i.e., the distance (and presumably the repulsion) between adjacent iodine atoms in the HCI_3 molecules remains nearly unchanged although the I–C–I angle is reduced. In fact, the average intramolecular I···I distance of the HCI_3 in the complexes (3.57 Å) is nearly identical with that in pure HCI_3 (3.56 Å).

Figure 4 displays the ciscoid conformation of the azulene bis(ammonium) units in the complex 4·2 HCI_3 and the linkage of the HCI_3 molecules with I^- ions. 50% of the iodide ions are unsymmetrically surrounded ($I \cdots I^- \cdots I$ angles see Table III), each by three iodine atoms of different HCI_3 molecules, approximately 3.5 Å distant.[19] The other iodide ions are flanked by an azulene ring plane and the two ammonium side chains, whereby only two HCI_3 molecules are neighbored. On the other hand, the triiodomethane units are surrounded by iodide ions. The coordination number is two or three, each to 50%; i.e., one sixth of the

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[17] Iwata, Y.; Watanabe, T. *Annu. Rep. Res. React. Inst., Kyoto Univ.* **1974**, *7*, 87–83; *Chem. Abstr.* **1975**, *82*, 148611p.

[18] On complex formation of uncharged n-donors and triiodomethane, the charge is transferred from the donor to the antibonding σ^* orbital or to the sp^3d-hybrid orbital of the iodine atom.[9] Hence, in both cases a linear donor···I–C arrangement will offer a maximum of orbital overlapping and bond strength.

[19] A fourth triiodomethane molecule is 4.10 Å distant apparently, somewhat less than the van der Waals sum of 4.35 Å. The correspondent $I^- \cdots I$–C angle amounts only to 152.1°.

[20] Johnson, C. K. ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge, 1965; extended by R. Hundt, Bonn, 1969.

Table II. Crystallographic Data of Complexes $4 \cdot 2\ HCI_3$, $8 \cdot 2\ HCI_3$, and $19 \cdot HCI_3$

	$4 \cdot 2\ HCI_3$	$8 \cdot 2\ HCI_3$	$19 \cdot HCI_3$
crystal dimensions (mm)	0.20 × 0.10 × 0.06	0.40 × 0.30 × 0.10	0.35 × 0.22 × 0.15
shape	columns	plates	plates
color	red violet	light yellow	light yellow
formula	$C_{20}H_{32}I_2N_2 \cdot 2\ HCI_3$	$C_{18}H_{34}I_2N_2 \cdot 2\ HCI_3$	$C_9H_{14}IN \cdot HCI_3$
mole mass (g mol^{-1})	1341.76	1319.72	656.84
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Cc	Pc
unit cell: a (pm)	1604.3 (8)	1353.5 (6)	990.8 (3)
b (pm)	1213.7 (6)	1642.5 (3)	739.5 (1)
c (pm)	1836.0 (7)	1610.0 (2)	1380.8 (2)
β (deg)	100.06 (3)	93.13 (3)	123.38 (2)
V (nm^3)	3.520	3.574	0.846
formula units Z	4	4	2
d (g cm^{-3})	2.53	2.45	2.58
F_{000}	2416	2376	588
absorption μ (cm^{-1})	66.1	65.1	68.9
range	1° < θ < 25°	1° < θ < 25°	1° < θ < 27°
observed reflections (with $\sigma(I)/I < 2$)	3970	3053	1576
refined parameters	169	159	134
R	0.063	0.059	0.057
R_w		0.063	0.054

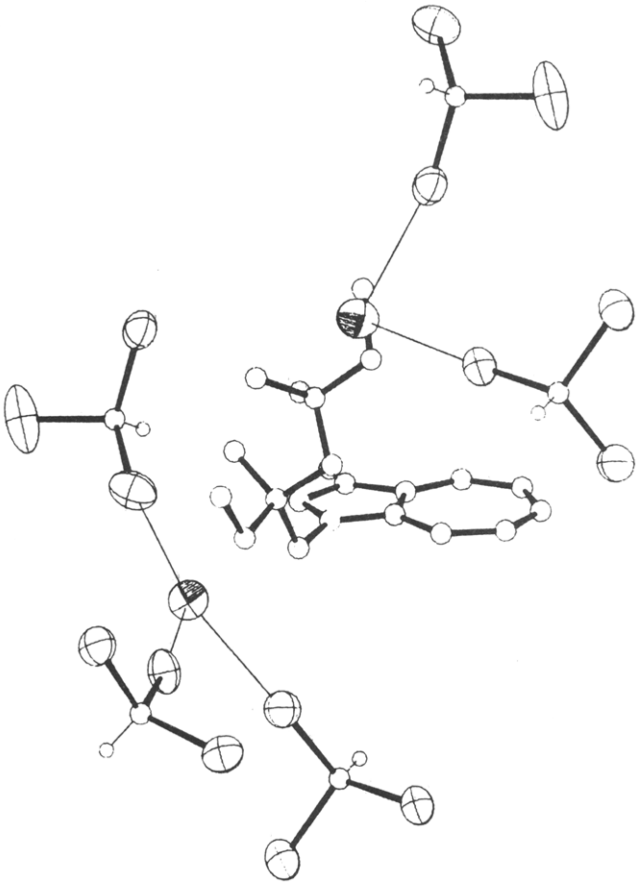

Figure 4. ORTEP drawing[20] of the bis(ammonium) salt **4** with coordinated HCI_3 molecules in their charge-transfer complex (iodide ions with shaded octants).

iodine atoms of HCI_3 is not involved in charge transfer interactions.

A larger section of the unit cell (Figure 5) shows the positions of the azulene units toward each other and displays the three-dimensional connection of the HCI_3 molecules by the iodide ions.

Figure 6 indicates the $I^- \cdots HCI_3$ linkage in the complex **19**·HCI_3. In this case every iodide ion as well as every triiodomethane is connected three times by electron donor–acceptor bonds.

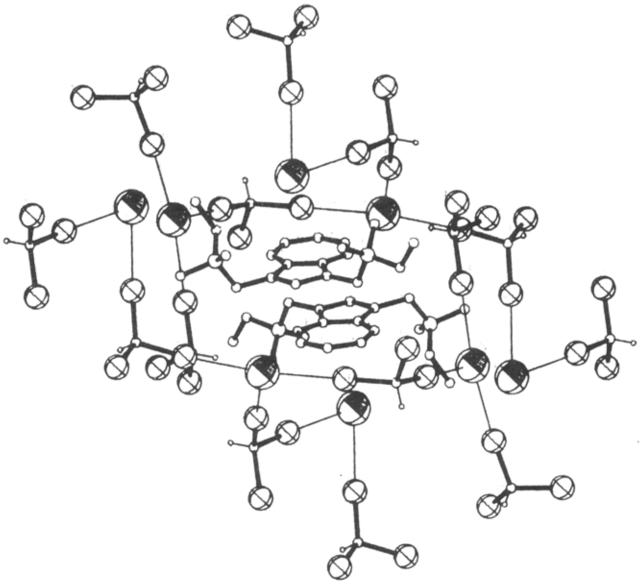

Figure 5. Section of the unit cell of the complex **4**·2 HCI_3 (iodide ions with shaded octants).

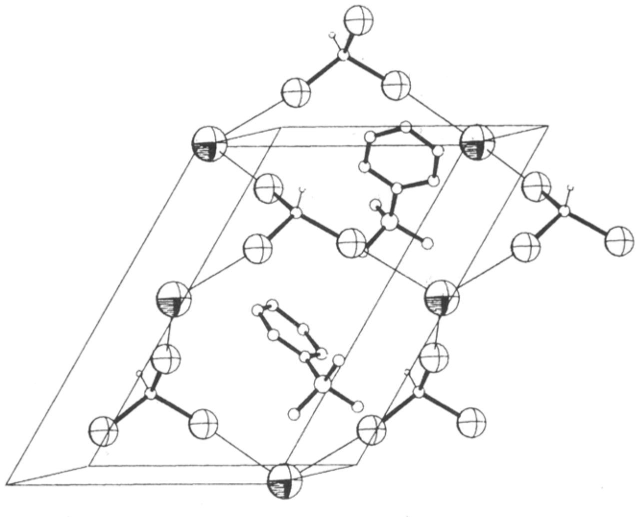

Figure 6. Unit cell of the complex **19**·HCI_3 (iodide ions with shaded octants).

In contrast to the complexes **4**·2 HCI_3 and **19**·HCI_3, we found in the **8**·2 HCI adduct (Figure 7) that only one half of the iodide ions is coordinated with approximately 3.6 Å distance, each by two acceptor molecules. The other half of the I^- ions is more than 4.35 Å distant from the next

Table III. Selected Bond Lengths and Angles of the Charge Transfer Complexes 4·2 HCI_3, 8·2 HCI_3, and 19·HCI_3

complex	bond lengths, pm		bond angles, deg	
4·2 HCI_3	I(1)···I(3)	347.1 (2)	I(1)···I(3)-C(21)	174.9 (4)
	I(1)···I(5)	347.8 (2)	I(1)···I(5)-C(21)	178.3 (7)
	I(1)···I(7)	353.4 (2)	I(1)···I(7)-C(22)	168.3 (4)
	I(1)···I(8)	410.4 (2)	I(1)···I(8)-C(22)	152.1 (5)
	I(2)···I(4)	369.0 (2)	I(2)···I(4)-C(21)	173.1 (4)
	I(2)···I(6)	346.6 (2)	I(2)···I(6)-C(22)	170.8 (4)
	I(3)···I(4)	356.8 (2)	I(3)···I(1)···I(5)	100.53 (5)
	I(3)···I(5)	354.4 (2)	I(3)···I(1)···I(7)	146.13 (5)
	I(4)···I(5)	358.0 (2)	I(3)···I(1)···I(8)	81.85 (4)
	I(4)···I(6)	417.5	I(5)···I(1)···I(7)	110.82 (5)
	I(6)···I(7)	353.1 (2)	I(5)···I(1)···I(8)	171.09 (6)
	I(6)···I(8)	355.0 (2)	I(7)···I(1)···I(8)	69.17 (4)
	I(7)···I(8)	362.7 (3)	I(4)···I(2)···I(6)	71.32 (4)
	C(21)-I(3)	220 (2)	I(3)-C(21)-I(4)	110.5 (8)
	C(21)-I(4)	214 (2)	I(3)-C(21)-I(5)	109.0 (6)
	C(21)-I(5)	215 (2)	I(4)-C(21)-I(5)	113.3 (7)
	C(22)-I(6)	213 (2)	I(6)-C(22)-I(7)	110.8 (7)
	C(22)-I(7)	216 (2)	I(6)-C(22)-I(8)	111.6 (8)
	C(22)-I(8)	216 (2)	I(7)-C(22)-I(8)	114.0 (8)
8·2 HCI_3	I(1)···I(4)	354.6 (3)	I(1)···I(4)-C(19)	169.2 (5)
	I(1)···I(6)	360.6 (3)	I(1)···I(6)-C(20)	172.5 (6)
	I(3)···I(7)	400.9	I(4)···I(1)···I(6)	119.52 (5)
	I(3)···I(8)	425.2		
	I(3)···I(4)	357.1 (2)		
	I(3)···I(5)	352.8 (2)		
	I(4)···I(5)	356.8 (3)		
	I(4)···I(8)	383.2		
	I(5)···I(8)	432.5		
	I(6)···I(7)	362.2 (3)		
	I(6)···I(8)	354.9 (3)		
	I(7)···I(8)	349.6 (3)		
	C(19)-I(3)	207 (2)	I(3)-C(19)-I(4)	112.4 (9)
	C(19)-I(4)	223 (2)	I(3)-C(19)-I(5)	113.4 (9)
	C(19)-I(5)	215 (2)	I(4)-C(19)-I(5)	109.2 (9)
	C(20)-I(6)	215 (2)	I(6)-C(20)-I(7)	112.1 (8)
	C(20)-I(7)	222 (2)	I(6)-C(20)-I(8)	113.2 (9)
	C(20)-I(8)	210 (2)	I(7)-C(20)-I(8)	107.9 (9)
19·HCI_3	I(1)···I(2)	365.6 (2)	I(1)···I(2)-C(10)	167.1 (4)
	I(1)···I(3)	367.3 (2)	I(1)···I(3)-C(10)	175.2 (4)
	I(1)···I(4)	358.3 (1)	I(1)···I(4)-C(10)	179.6 (4)
	I(2)···I(3)	360.2 (3)	I(2)···I(1)···I(3)	119.55 (4)
	I(2)···I(4)	359.2 (2)	I(2)···I(1)···I(4)	89.59 (4)
	I(2)···I(5)	353.7 (2)	I(3)···I(1)···I(4)	111.85 (4)
	C(10)-I(2)	211 (2)	I(2)-C(10)-I(3)	112.9 (6)
	C(10)-I(3)	222 (1)	I(2)-C(10)-I(4)	111.9 (8)
	C(10)-I(4)	216 (1)	I(3)-C(10)-I(4)	110.2 (7)

triiodomethane. Each HCI_3 molecule is single bonded via one iodine atom to an I^- ion. Therefore two thirds of the HCI_3 iodine atoms are not involved in donor–acceptor interactions in this complex. Consequently in this case, and in contrast to the two described HCI_3 complexes above, isolated I^- ions beside I^-·2 HCI_3 units are present. The effect of the bulky *tert*-butyl group on the molecular packing might be responsible for this behavior. The shortest HCI_3···HCI_3 distances in this complex range about 3.83 Å, resembling the intermolecular I···I distances in solid triiodomethane (3.98 Å).

Raman Spectra. Table IV indicates the Raman bands of pure triiodomethane[21] and a few of its complexes below 700 cm^{-1}. Some typical spectra are illustrated in Figure 8. A great part of the complexes could not be examined because of rapid decomposition by the excitation radiation.

All fundamental modes of the HCI_3 molecule are Raman active (cf. ref 10). The two low-frequency bands are assigned to the symmetric (ν_3, 153 cm^{-1}) and degenerate (ν_6, 109 cm^{-1}) CI_3 deformation. The bands at 430 cm^{-1} (ν_2, s) and 577 cm^{-1} (ν_5, d) belong to the CI stretching. Some complexes show a splitting of the doubly degenerate modes of triiodomethane. Mostly the bands are shifted from their positions in pure HCI_3. This can be explained by a reduction of the local symmetry of the HCI_3 molecules due to iodine atoms involved in charge-transfer interactions. As seen from the X-ray analyses, the HCI_3 symmetry in

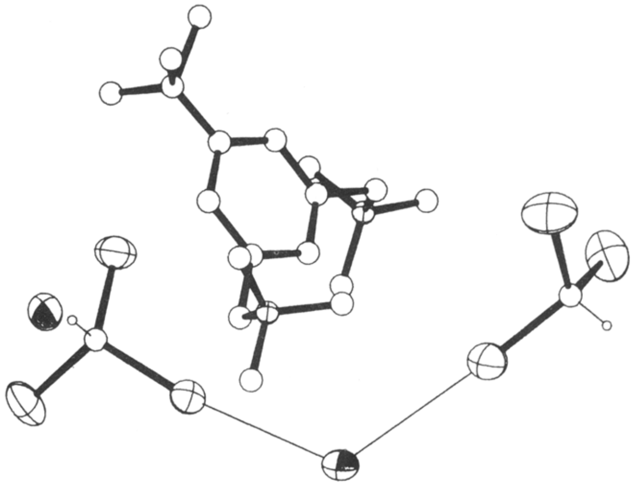

Figure 7. Section of the unit cell of the complex 8·2 HCI_3 (iodide ions with shaded octants).

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[21] Schrader, B.; Meier, W. "Raman-IR-Atlas of Organic Compounds"; Verlag Chemie: Weinheim, 1978; Vol 1.

Table IV. Raman Spectra of Crystalline Triiodomethane and Its Complexes (700–20 cm^{-1})

compd[a]	ν_5 (E)	ν_2 (A$_1$)	ν_3 (A$_1$)	ν_6 (E)	other bands
pure HCI$_3$	577 ms	430 ms	153 s	109 s	33 ms, 40 sh
6·3 HCI$_3$	565 m	433 m	156 s	113 ms, 101 ms	31 vs
8·2 HCI$_3$	578 m, 573 sh	430 m	153 s	109 ms	43 ms, 58 m
13·2 HCI$_3$	571 ms	432 m	151 s	114 m	36 ms
17·2 HCI$_3$	568 ms, 574 sh	427 m	146 s	107 ms	21 s, 30 sh, 44 sh
19·HCI$_3$	574 ms, 566 ms	437 ms	153 s	111 ms, 115 sh	49 s
20·4 HCI$_3$	566 ms	441 m	154 s	110 ms	21 s, 30 sh, 40 sh
21·2 HCI$_3$	576 m	432 m	153 s	110 ms	
25·2 HCI$_3$	571 m	435 m	152 s	107 ms	

[a] The other triiodomethane complexes synthesized could not be examined because of rapid decomposition.

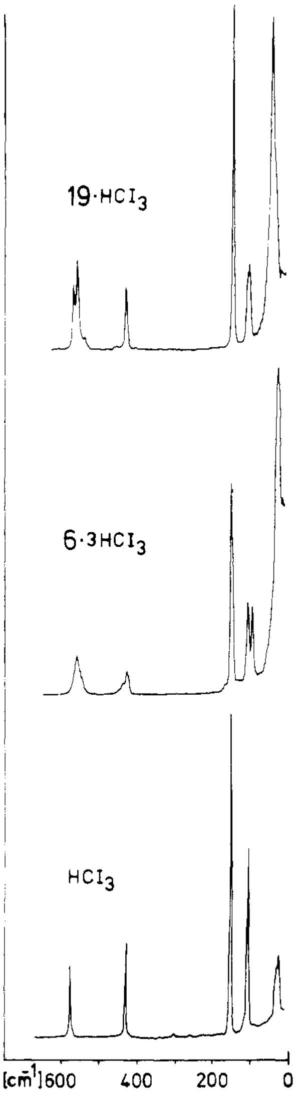

Figure 8. Raman spectra of triiodomethane and two of its complexes (20–600 cm^{-1}).

the complexes **4**·2 HCI$_3$ and **8**·2 HCI$_3$ is modified from C_{3v} (CXY$_3$) to C_s (CXYZ$_2$).

Some HCI$_3$ complexes show Raman bands in the frequency range below 100 cm^{-1}, which do not appear in the spectra of the pure components. Because of the high intensities, the bands may be associated with crystal-lattice modes having a large amplitude of the I$^-$···HCI$_3$ stretching.

NMR Data of I$^-$···HCI$_3$ Complexes in Solution. HCI$_3$ in acetonitrile shows an increased shielding in the ^{1}H NMR spectrum on addition of tetraalkylammonium halides.[12] This observation is in accordance with the expected charge transfer from the iodine ion to the HCI$_3$ molecule, which tends to shield the acceptor molecule. On the contrary, we found in the ^{13}C NMR spectra of the complexes **4**·2 HCI$_3$, **8**·2 HCI$_3$, and **19**·HCI$_3$ in solution (0.223 M in Me$_2$SO-d_6) a significant deshielding of about 10 ppm for the haloform carbon nucleus in comparison with pure HCI$_3$.[22] This deshielding is—considering the expected increase of electron density—anomalous.

The strong shielding of the HCI$_3$ carbon is attributed to the symmetric distribution of the three electron-rich iodine atoms around the carbon nucleus. The interaction of iodide ions with iodine atoms of HCI$_3$ effects a slight lengthening of the C–I bonds and a reduction of the I–C–I bond angles (see above). The diminishing of the I–C–I angles and the C–I lengthening tend to *de*crease the influence of the adjacent iodine atoms and therefore *de*shield the carbon nucleus. Presumably, this effect prevails the EDA bond dependent increase of electron density.

The determination of the equilibrium constant for the charge-transfer reaction of iodide with triiodomethane by the Benesi–Hildebrand–Scott method (see Experimental Section) yielded $K = 2.00 \pm 0.28$ L/mol in Me$_2$SO-d_6. The limiting shift value was calculated to $\Delta_c = 31.5 \pm 3.0$. Our value of K is about of the same magnitude as that deduced by Green and Martin[12] for tetrabutylammonium iodide and triiodomethane in acetonitrile ($K = 3.56$ L/mol). The difference might be referred to the higher polarity of dimethyl sulfoxide.

Conclusion

A series of well-defined, crystalline organylammonium iodide complexes with triiodomethane were prepared. The different spectroscopic investigations indicate that iodide ions and triiodomethane molecules are associated by charge-transfer interactions in the solid state as well as in solution. It is observed from the X-ray analyses of three complexes that the I$^-$···HCI$_3$ distances are distinctly shorter than the sum of the appropriate van der Waals radii. Since each I$^-$ as well as each HCI$_3$ unit can be linked one, two, or three times, the crystal lattices are built up in different manners. Whether the charge-transfer interactions result in space networks or smaller I$^-$···HCI$_3$ units is presumably induced by crystal-packing effects.

From Raman spectra it is found that charge-transfer association, although weak, can readily destroy the local symmetry of molecules like HCI$_3$ and can cause distinct frequency shifts and band splittings.

^{13}C NMR spectra in Me$_2$SO-d_6 as solvent indicate a significant downfield shift for the signal of the HCI$_3$ carbon nucleus, on addition of ammonium iodides. This deshielding is probably caused by the reduction of the I–C–I

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[22] The chemical shift values of the HCI$_3$ carbon nucleus of 0.223 M complexes and triiodomethane in Me$_2$SO-d_6 at 298 K are: δ [ppm] HCI$_3$ −139.8; **4**·2 HCI$_3$ −130.4; **8**·2 HCI$_3$ −128.3; **19**·HCI$_3$ −130.9.

angles, if I$^-$ donor ions are associated. The complex formation constant has been determined from the chemical shift of the HCI$_3$ carbon nucleus as a function of the iodide ion concentration by the Benesi–Hildebrand–Scott method. The value of K = 2.0 L/mol assigns the complex being relatively weak in solvents of this type.

No charge-transfer bands were observed in the absorption spectra of the complexes in solution (acetonitrile, methanol).[23] Consideration of the diffuse reflectance of solid complexes also gave unsatisfactory results because of very broad absorption bands in the near UV.

The specific electrical conductivities of the triiodomethane complexes in the solid state range at the lower end of the semiconductor region. Although it is not simple to associate the conductivities with structural properties, it is interesting that the specific conductivity in the sequence 8·2 HCI$_3$ < 4·2 HCI$_3$ < 19·HCI$_3$ increases with the extent of the three-dimensional I$^-$···HCI$_3$ linkages.

Further studies of detailed structures, in connection with conductivity measurements, will show if electrical and structural properties can be correlated in this type of charge-transfer complex.

Acknowledgment. We thank Prof. Dr. W. Swodenk and Dr. J. Hocker, Bayer AG, Leverkusen, for the electrical conductivity measurements, Dipl.-Chem. W. Wald for recording the Raman spectra, and Ing. C. Schmidt for the ^{13}C NMR measurements.

Registry No. 1·2HCI$_3$, 88791-65-5; 2·2HCI$_3$, 88791-77-9; 3, 88888-16-8; 4·2HCI$_3$, 88791-78-0; 5·HCI$_3$, 88791-79-1; 6·3HCI$_3$, 88791-82-6; 7, 88888-17-9; 8·2HCI$_3$, 88888-02-2; 9, 88888-18-0; 10, 88888-19-1; 11, 88888-20-4; 12, 88888-21-5; 13·2HCI$_3$, 88888-04-4; 14·HCI$_3$, 88888-05-5; 16·2HCI$_3$, 88791-94-0; 17·2HCI$_3$, 88888-06-6; 18·4HCI$_3$, 88791-92-8; 19·HCI$_3$, 88888-07-7; 20·4HCI$_3$, 88888-08-8; 21·2HCI$_3$, 88888-10-2; 24·$^1/_2$HCI$_3$, 88888-12-4; 25·2HCI$_3$, 88888-14-6; HCI$_3$, 75-47-8.

Supplementary Material Available: Bond lengths and angles, atomic coordinates, and thermal parameters of the complexes 4·2 HCI$_3$, 8·2 HCI$_3$, and 19·HCI$_3$ (11 pages). Ordering information is given on any current masthead page.

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[23] A possible increase of the n → σ^* absorption intensities of HC$_3$,[24,25] on addition of organylammonium or potassium iodide, can be referred to the formation of triiodide I$_3^-$ from I$_2$ traces. In presence of sodium thiosulfate in methanol the absorption spectrum of HCI$_3$ remains unchanged (above 280 nm) if iodides are added.

(24) Ito, M.; Huang, P.-K. C.; Kosower, E. M. *Trans. Faraday Soc.* **1961**, *57*, 1662–1673.

(25) Kimura, K.; Nagakura, S. *Spectrochim. Acta* **1961**, *17* 166–183.

Syntheses and Structures of Stilbene Cycles. 2. Low-Valent Titanium-Induced Ring Closures of Aromatic Bis(carbonyls)[1]

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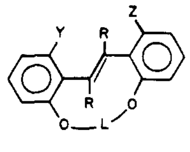
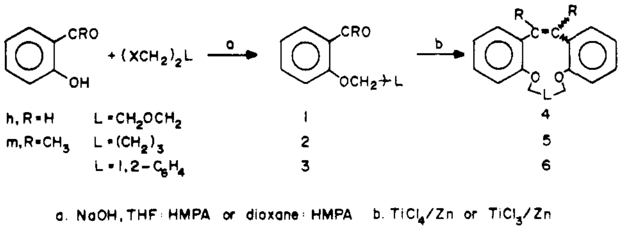
Low-valent titanium-induced reductive coupling has been used to prepare stilbene cycles. Bis(carbonyl) ethers, **1h**-**3h** and **1m**-**3m**, have been prepared from the reactions of salicylaldehyde (**h**) and 2-hydroxyacetophenone (**m**) with diethylene glycol ditosylate (**1**), 1,5-dibromopentane (**2**), and 1,2-xylylene dibromide (**3**) in HMPA/dioxane or THF, in the presence of NaOH. Bis(carbonyl) ethers, **1h**, **1m**, **2h**, and **2m**, have been cyclized with TiCl$_4$/Zn or TiCl$_3$/Zn in dioxane to give *E* and *Z* isomers of dibenzo[*a*,*e*]-7,10,13-trioxa- and -7,13-dioxacyclotrideca-1,3,5-trienes, **4h**, **4m**, **5h**, and **5m**, respectively. Compound **3h** under these conditions is not transformed into a cycle but rather forms (*E*)-1,2-bis(2-hydroxyphenyl)ethene, (*E*)-**7h**. Compound **3m** is cyclized but only (*Z*)-**6m** is isolated. Photoisomerization of (*Z*)-**6m** gives (*E*)-**6m** as the predominant isomer. Crystal structures are reported for (*Z*)-**4h**, (*Z*)-**4m**, (*E*)-**5h**, (*Z*)-**6m**, (*E*)-**6m**, and (*E*)-**7h**.

Introduction

Development of new chemical models for enzymatic catalysis is the long-range goal of research efforts in these laboratories. Designs of new models have focused on developing a moderately rigid backbone on which to anchor reacting groups in arrangements approximating those found in enzyme active sites. Stilbene cycles appear to satisfy many of the design criteria. The bridging unit, L, serves to restrict Y and Z to lie on the same side as well as control the relative conformation of the two benzenoid rings.



Scheme I



A preliminary report from these laboratories[2] has outlined a convenient high yielding synthetic method (Scheme I) for the preparation of this class of compounds. The preparation of the bis(carbonyl) ethers in high yields is particularly noteworthy in the light of previously reported methods.[3] The good yields for the cyclization are expected

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(1) This work is supported by a grant from NIGMS, GM29128. J. T.-R. acknowledges the CONACYT of Mexico for financial support.

(2) Tirado-Rives, J.; Gandour, R. D.; Fronczek, F. R. *Tetrahedron Lett.* **1982**, *23*, 1639–1642.

0022-3263/84/1949-1627$01.50/0