

Tricyclic Germanium Heterocycles: The Structure of 5,5-Diphenyl-10,11-dihydro-5*H*-dibenzo[*b,f*]germepin and the Mass Spectroscopic Analysis of 5,5-Dimethyl- and 5,5-Diphenyl-10,11-dihydro-5*H*-dibenzo[*b,f*]germepin and Their Unsaturated Analogs (I)

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Before 1971 two reports appeared in the literature for the synthesis of tricyclic derivatives with a central seven-membered ring containing a Group IV heteroatom (3,4). Since that time we have reported the synthesis of substituted 10,11-dihydrodibenzo[*b,f*]metallepins of Group IV (5,6). The entire series of derivatives with $M = \text{Si, Ge, Sn, Pb}$ and $R = \text{CH}_3$ or C_6H_5 has been obtained. The dibenzo[*b,f*]metallepins of silicon and germanium were prepared by bromination of the 10,11-dihydrodibenzo[*b,f*]metallepins followed by dehydrobromination with diazabicyclononene (6). Since this work was reported 5,5-dimethyldibenzo[*b,f*]silepin has been prepared by other workers by 1) dehydrogenation of the saturated system with dichlorodicyanoquinone in boiling toluene (7) and, 2) dibromination of the saturated system with NBS followed by debromination with zinc (8). Because aryl-Sn and aryl-Pb compounds are cleaved by NBS, the stannepin and plumbepin analogs are inaccessible by any of these routes.

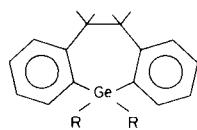
Few studies appear in the literature on the mass spectral characteristics of organogermanium heterocycles (9,10), and no solid state structural studies have been reported for tricyclic systems containing a group IV heteroatom. X-ray diffraction studies have been reported for tricyclic systems with a central seven-membered ring containing only carbon, e.g., 3-chloro-5-(3-dimethylaminopropylidene)-5*H*-dibenzo[*a,d*]cycloheptene (11), 3-(10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene)-1-ethyl-2-methylpyrrolidine hydrobromide (12), 5-(bromoethylene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (13), dibenzo[*b,f*]tropone (14) and dimethoxysuberone (15). This report describes a solid state structural study of 5,5-diphenyl-10,11-dihydro-5*H*-dibenzo[*b,f*]germepin (Ia) and a detailed mass spectroscopic analysis of Ia, 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b,f*]germepin (Ib), 5,5-diphenyl-5*H*-dibenzo[*b,f*]germepin (IIa) and 5,5-dimethyl-5*H*-dibenzo[*b,f*]germepin (IIb).

TABLE I. INTERATOMIC BOND DISTANCES(Å) AND ANGLES(°)

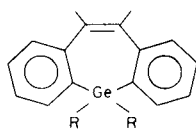
Angle	Value (°)	Angle	Value (°)
1-Ge-7	114.8 (.5)	3-4-5	121.7(1.6)
1-Ge-13	108.5 (.5)	4-5-6	121.5(1.6)
1-Ge-19	109.0 (.5)	5-6-7	119.0(1.4)
7-Ge-13	106.9 (.5)	6-1-2	118.5(1.2)
7-Ge-19	109.3 (.5)	7-8-9	117.2(1.3)
13-Ge-19	108.1 (.4)	8-9-10	122.3(1.5)
Ge-1-2	118.0 (.9)	9-10-11	122.5(1.5)
Ge-1-6	123.5(1.0)	10-11-12	115.9(1.4)
Ge-7-8	122.7 (.9)	11-12-7	122.9(1.2)
Ge-7-12	118.1 (.9)	12-7-8	119.1(1.2)
Ge-13-14	120.6 (.8)	13-14-15	120.3(1.1)
Ge-13-18	119.2 (.9)	14-15-16	120.0(1.4)
Ge-19-20	121.3 (.9)	15-16-17	120.7(1.3)
Ge-19-24	120.8 (.9)	16-17-18	122.0(1.2)
1-6-26	121.2(1.6)	17-18-13	116.8(1.2)
5-6-26	118.8(1.6)	18-13-14	120.0(1.0)
7-8-25	119.5 (b)	19-20-21	117.9(1.1)
9-8-25	119.7 (b)	20-21-22	121.4(1.3)
8-25-26	120.4 (b)	21-22-23	122.1(1.7)
6-26-25	114.0 (b)	22-23-24	120.5(1.6)
1-2-3	120.0(1.1)	23-24-19	120.2(1.3)
2-3-4	119.2(1.4)	24-19-20	117.8(1.2)

(a) Estimated standard deviations for bond distances are 0.01Å for Ge-C, 0.02Å for C-C; estimated standard deviations for the angles are enclosed in parentheses.

(b) Estimated standard deviations for bond distances and angles that involve atom 25 have not been assigned because the final model was unable to account for the apparent disorder of this atom.



Ia: R = C₆H₅
b: R = CH₃



IIa: R = C₆H₅
b: R = CH₃

TABLE II. RELATIVE INTENSITIES OF FRAGMENTS IN THE CALCULATED MONOISOTOPIC SPECTRA GENERATED FROM Ia,b AND IIa,b

m/e(a)	Ia	IIa	Ib	IIb
76				2.4*
77			6.1*	
89			26	35
91	23*	3.4*	2.6*	
104			8.2*	9.0
105	64*			
151	6.4	91.5	8.5	3.5
152	8.7(c)	4.7	3.3*	4.4
163			4.2	
164			1.7	
165	25*		1.0*	
178	100*	35.2*	34*	100*
179	30*	8.1*	20*	4.8*
180	21*		6.1*	
189				2.9*
191			4.0	2.5*
192			1.5	
193			2.1	
224				1.0
225			1.7	6.0
226	18	18.6	1.3	1.2
227	30	46.5		
228	100	100		
249				3.3
250			1.3	3.6
251			2.7	8.8
252	12	11*		
253	24	9.9*	1.6	
254		34.7*(d)		
267			17	77(e)
269			100	
281				3.5
282				27
284			29	
328		3.1		
329		10.7		
330	60			
331	76			
405		3.6		
406		59		
408	12			

- (a) Corrected for the abundance of C¹³. The following isotopic distribution for germanium was used to calculate the spectra: 76(21), 74(100), 73(21), 72(75), 70(57). All m/e values recorded for metal-containing fragments are based on the 74 isotope.
 (b) Fragments less than 1% of the base peak are not recorded.
 (c) Overlapping organic fragments: 149(6.5), 152(6.5).
 (d) 255*(5.2).
 (e) Base peak at 15eV.

Single crystal x-ray diffraction techniques have shown that the solid state structure of Ia is composed of individual molecular species with the tricyclic ring system in a boat conformation (Figure 1). The angle formed by the intersection of the planes of the two benzo groups is 156°. The angles formed by the intersections of the benzo group planes and the plane defined by the atoms common to the benzo groups and the central ring (C₁, C₆-C₈) are 168° (C₁-C₆) and 166° (C₇-C₁₂). The benzo groups are not twisted relative to one another within experimental error.

TABLE III. METASTABLE SUPPORTED TRANSITIONS IN THE MASS SPECTRA OF Ia,b AND IIa,b

Compound	Metastable Observed	Assigned Transition(a)	Metastable Calculated(b)
Ia	65-71 77-79.5 125-129 188-194 200-204 264-268	331 + 151	66.1-70.3
		330 + 151	66.3-70.5
		408 + 180	79.0-80.2
		408 + 178	77.3-78.4
		408 + 228	124.1-129
		331 + 253	189.6-195.3
		330 + 252	188.7-194.3
		253 + 227	199.7-205.6
		252 + 226	198.7-204.7
		408 + 331	264.7-270.3
408 + 330	263.1-268.8		
IIa	66-70 77-79.5 124-130 157-161	328 + 151	66.7-70.9
		406 + 178	77.7-78.8
		406 + 228	124.8-130
		406 + 255	159.4-161.8
		406 + 254	158.1-160.5
		405 + 254	158.5-160.9
Ib	27.5-30.5 110-115 117-121	269 + 89	27.2-30.3
		284 + 180	112.4-114.9
		284 + 178	110.7-113.1
		269 + 180	119.5-122.3
		269 + 178	116.8-119.4
		129-131	127.5-133.0
		125-128	124.8-130.1
		197-203	197.6-203.4
IIb	27.5-30.5 111-115 128-131 198-204 231-239 248-255	269 + 267	261.0-267.0
		267 + 89	27.5-30.8
		282 + 178	111.6-114.0
		282 + 191	128.5-131.2
		251 + 226	199.5-205.5
		267 + 251	232.0-238.0
282 + 267	248.8-254.7		

- (a) Transitions are given for Ge⁷⁴ (see TABLE II).
 (b) Metastables were calculated for the range of Ge isotopes for each transition.
 (c) Overlaps with Ge fragment.

Table I lists the interatomic bond distances and angles with estimated standard deviations. The bond distances and angles are normal except for those that involve carbon atom 25. As explained in the experimental section, a disorder in this atom has prevented the assignment of a completely satisfactory final model for the structure. The mean Ge-C distance of 1.95Å agrees well with the value of 1.93Å obtained by correction of the sum of the germanium and carbon single bond radii for the electronegativity difference of the atoms (16).

In Table II are recorded the abundances of the fragments produced in the mass spectra of the dihydrodibenzo[*b,f*]germepins and the dibenzo[*b,f*]germepins. The data have been reduced to monoisotopic form and corrected for C¹³. The most abundant isotope of

TABLE IV. FINAL POSITIONAL AND THERMAL PARAMETERS FOR Ia

Atom	X	Y	Z	B(Å ²)
Ge	0.2155(1)	0.2110(2)	0.07818(5)	4.22(4)
C ₁	0.354 (1)	0.326 (1)	0.1130 (5)	5.3 (2)
C ₂	0.448 (1)	0.363 (2)	0.0698 (6)	6.3 (3)
C ₃	0.556 (1)	0.437 (2)	0.0942 (7)	7.8 (3)
C ₄	0.563 (1)	0.475 (2)	0.1582 (8)	7.8 (3)
C ₅	0.477 (2)	0.441 (2)	0.1998 (8)	8.9 (4)
C ₆	0.368 (1)	0.366 (2)	0.1785 (7)	8.0 (3)
C ₇	0.056 (1)	0.231 (1)	0.1236 (6)	5.9 (2)
C ₈	0.052 (1)	0.269 (2)	0.1915 (7)	7.4 (3)
C ₉	-0.070 (2)	0.274 (2)	0.2196 (8)	8.3 (4)
C ₁₀	-0.175 (2)	0.244 (2)	0.1850 (8)	8.2 (4)
C ₁₁	-0.176 (2)	0.204 (2)	0.1180 (8)	8.2 (4)
C ₁₂	-0.055 (1)	0.199 (2)	0.0890 (7)	7.0 (3)
C ₁₃	0.179 (1)	0.258 (1)	-0.0166 (5)	4.7 (2)
C ₁₄	0.135 (1)	0.386 (1)	-0.0344 (5)	5.8 (2)
C ₁₅	0.106 (1)	0.417 (2)	-0.1010 (6)	6.5 (3)
C ₁₆	0.118 (1)	0.320 (2)	-0.1487 (6)	6.3 (3)
C ₁₇	0.160 (1)	0.196 (2)	-0.1328 (6)	6.4 (3)
C ₁₈	0.191 (1)	0.158 (1)	-0.0655 (6)	5.5 (2)
C ₁₉	0.269 (1)	0.022 (1)	0.0825 (5)	4.6 (2)
C ₂₀	0.399 (1)	-0.014 (1)	0.0814 (5)	5.6 (2)
C ₂₁	0.431 (1)	-0.156 (2)	0.0821 (6)	6.6 (3)
C ₂₂	0.343 (1)	-0.249 (2)	0.0812 (6)	6.6 (3)
C ₂₃	0.218 (1)	-0.218 (2)	0.0838 (6)	6.4 (3)
C ₂₄	0.179 (1)	-0.084 (2)	0.0837 (6)	6.1 (3)
C ₂₅	0.176 (2)	0.358 (3)	0.2283(11)	12.2 (6)
C ₂₆	0.281 (3)	0.310 (3)	0.2309(13)	14.2 (7)

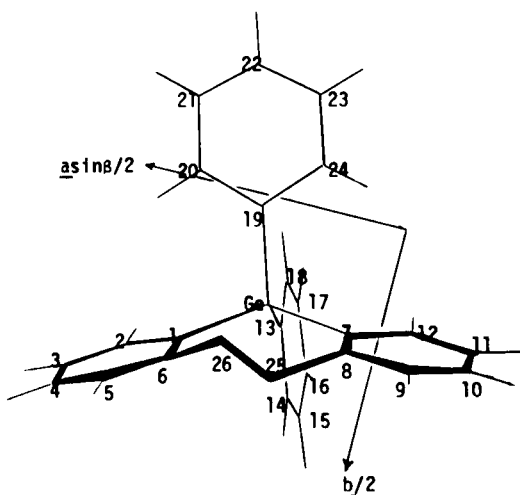
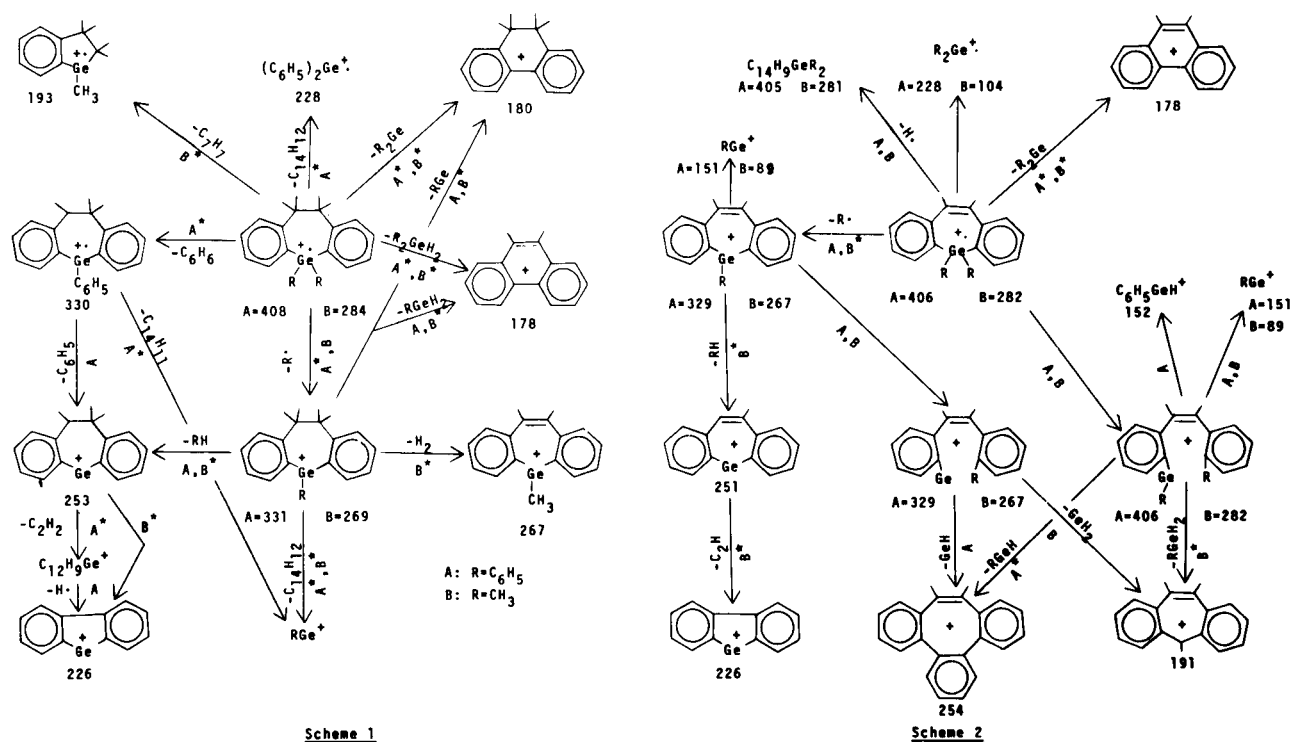


Figure 1. The Molecular Configuration of 5,5-Diphenyl-10,11-dihydro-5H-dibenzo[b,f]-germepin

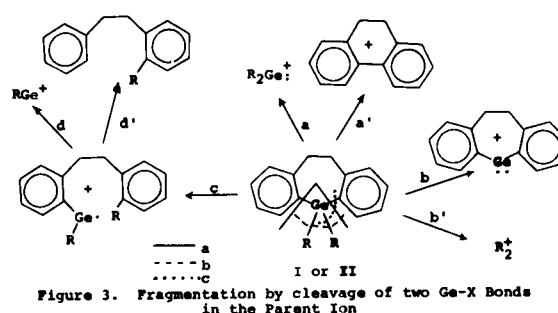
germanium, Ge⁷⁴, is used to represent a germanium fragment. Fragments that do not contain a germanium atom are marked with an asterisk. A plausible rationalization for the origin of the principal ions produced in the mass spectrum of both the saturated and unsaturated germepins is outlined in Figure 2 as Schemes 1 and 2, respectively. All metastables observed in the spectra are listed in Table III with an assigned transition.

In a recent study (6) we showed that the majority of the fragments produced from dihydrodibenzo[b,f]metallepins upon electron impact resulted from one of three types of processes: 1) cleavage of an exocyclic bond to eliminate an odd-electron radical, *cf.*, elimination of C₆H₅[·] from the molecular ion of Ia and CH₃[·] from the molecular ion of Ib; 2) elimination of a neutral molecule generally by cleavage of an exocyclic bond and abstraction of a hydrogen atom from the ethylene bridge, *cf.*, elimination of C₆H₆ from the molecular ion of Ia; 3) elimination of a neutral molecule by cleavage of two germanium ring bonds with charge retention either on the metal fragment or on the organic fragment.

Fragmentation of the parent ions of Ia and IIa by cleavage of an exocyclic bond, *i.e.*, C₆H₅[·], competes with loss of neutral benzene, C₆H₆, as is indicated by the fragments at *m/e* = 331 and 330. In the 15eV spectrum of Ia the abundance of the ion at *m/e* = 330 due to the loss of benzene has increased relative to that at *m/e* = 331 due to loss of a phenyl radical, which supports the direct loss of benzene from the parent ion rather than loss of a hydrogen atom followed by loss of phenyl. We have shown that the elimination of benzene in saturated 5-phenyl-5H-dibenzo[b,f]silepins proceeds by abstraction of a proton from the ethylene bridge since 5-phenyl-5-methyl-10,11-dihydro-5H-dibenzo[b,f]silepin-10,10,11,11-d₄ loses exclusively C₆H₅D upon electron impact (17). It is probable that the saturated germepin, Ia, loses benzene by a similar 1,4-elimination and that this elimination may be characteristic of compounds that exhibit the boat conformation which has been shown for Ia in this study. The 1,4-elimination reaction has been observed in the mass spectra of 9-sila- and 9-germaan-thracenes (18), 10-alkylphenothiazines (19) and tetralin (20) which contain six-membered rings in the boat conformation. The ratio of loss of benzene to loss of phenyl, *i.e.*, C₆H₆/C₆H₅, from the parent ion of 5,5-diphenyl-10,11-dihydro-5H-dibenzo[b,f]metallepins ranges from 100:1 for Si to about 1:1 for Ge to 1:3 for Sn indicating a decrease in the importance of the 1,4-elimination. The decrease in 1,4-elimination may be due to either a flattening of the tricyclic ring system or lengthening of the metal-carbon bond, either of which increases the distance between the heteroatom substituent and the ethylene bridge.



The remaining intense fragments in the spectra of the saturated and unsaturated dibenzo[*b,f*]germepins result from a process related to cleavage of two Ge-X bonds in the parent ion and ions of the type R_3Ge^+ (see Schemes 1 and 2). The possible simultaneous cleavages of two Ge-X bonds are illustrated for the parent ions of saturated germepins in Figure 3. Processes *a*, *b* and *d* yield fragments with charge retention on the Ge-containing portion and processes *a'*, *b'* and *d'* give charge retention on the organic portion. Similar processes may be envisioned for the unsaturated germepins. Cleavage by route *c* yields an ion indistinguishable from the parent ion; its presence is inferred by subsequent decomposition *via* route *d*. Evidence for fragmentation by routes *b* or *b'* has not been detected in the spectra of Ia,b or IIa,b. Metastable support exists for both *a* and *a'* processes for Ia and IIa and *a'* for Ib but the fragment $(CH_3)_2Ge^+$ does not occur in the spectrum of Ib. No metastable support exists for the occurrence of route *c* for the saturated dibenzo[*b,f*]germepins, I, although a very weak ion occurs at $m/e = 257$ (less than 1% of base peak) in the spectrum of Ia which implies the occurrence of a *c* to *d'* transition. In contrast, however, the strongest metastable in the spectrum of IIa is associated with the transition $m/e = 406$ to $m/e = 254$ which is a loss of neutral C_6H_5GeH from the parent ion, and formation of an organic ion at $m/e = 254$. The ion for $m/e = 254$ is depicted as a cyclic ion in Scheme 2, however, an unequivocal structure cannot



be assigned because open-chain structures are also possible. For the unsaturated system the decomposition routes *d* and *d'* are replaced by *e* and *e'* to account for the loss of $RGeH_x$ ($x = 1,2$) from the rearranged parent ion. The relative abundances of ions produced in the 15eV spectrum of IIa are almost identical to those reported in Table II except for $m/e = 178$ (13% of base peak at 15eV) and $m/e = 151$ (34% of base peak at 15eV). The data support a one-step loss of $RGeH^{O+}$ from the parent ion. A corresponding fragmentation route *c* to *e'* also exists for IIb (see Scheme 2) with metastable support. A one-step loss of $C_{12}H_{10}^0$ from $(C_6H_5)_4Ge$ has also been reported (21). Elimination of neutral germanium species upon electron impact (*cf.* routes *a*, *b*, *d*, and *e*) are rare for noncyclic germanium compounds. Cleavage by routes *a* and *b* occur for 1,1-diphenyl-germacyclopentane-3,3,4,4-d₄ (9). No corresponding fragments resulting from *a'* and *b'* with

charge retention on the organic fragment are reported; this may be due to lack of possible charge delocalization for $\text{H}_2\text{CCD}_2\text{CD}_2\text{CH}_2$ (or its cyclic counterpart). Although the simultaneous cleavage of two Ge-X bonds occurs predominantly with involvement of the ring-Ge bonds, the conclusion that the ring bonds are weaker than the exocyclic bonds is invalid since the structural data indicate that the exocyclic and ring germanium to aryl carbon bonds are equivalent.

EXPERIMENTAL

Crystal Data.

Crystals of 5,5-diphenyl-10,11-dihydro-5H-dibenzo[*b,f*]germanin (Ia) are monoclinic with $a = 10.50(2)$, $b = 9.81(2)$, $c = 19.99(4)$, $\beta = 92^\circ 36' \pm 10'$, $V = 2057 \text{ \AA}^3$; space group, $\text{P}2_1/n$; $D_{\text{meas}} = 1.32 \text{ g. cm}^{-3}$, $D_{\text{calc}} = 1.31 \text{ g. cm}^{-3}$ for $Z = 4$. Multiple film equi-inclination Weissenberg data were obtained for reciprocal levels $h0\bar{l}h6\bar{l}$. The intensities of 2129 visually estimated reflections were used in the structure determination. A crystal of dimensions $0.06 \times 0.08 \times 0.16 \text{ mm}$ mounted with the long dimension parallel to the rotation axis was used for data collection. No absorption corrections were made; $\mu = 22.3 \text{ cm}^{-1}$ (Cu $K\alpha$, $\lambda = 1.542 \text{ \AA}$).

Structure Determination.

The structure was solved by conventional heavy atom techniques. The Ge atom position was derived from a three-dimensional Patterson synthesis. Structure factors calculated with the Ge atom trial coordinates resulted in a discrepancy factor ($R = \Sigma |F_o - F_c| / \Sigma |F_o|$) of 35%. Positions for all the carbon atoms were established from successive electron density difference maps. Full matrix least squares refinement of all non-hydrogen atoms with isotropic thermal parameters yielded a final discrepancy factor of 9.8%. Hydrogen atoms were included on carbon atoms 1 through 24 at distances of 1.0 \AA and with thermal parameters equal to those of the carbon atoms to which they were bonded. The Ge atom scattering factor curve was corrected for anomalous dispersion; all scattering factors were from the "International Tables for X-ray Crystallography" (22). Final positional and thermal parameters are given in Table IV. One of the methylene carbon atoms (C_{25}) refined to a position with chemically unreasonable bond distances and angles. A difference electron density map was calculated in which contributions from all atoms except the methylene groups were removed. Two electron density maxima were present in the methylene region at coordinates virtually identical with the reported least squares positions. The background in this region of the map is relatively high and the peaks are diffuse. An electron density synthesis from which all atom contributions were removed using the coordinates in Table IV shows two peaks greater than 1 e/\AA^3 . Both peaks (1.5 and 1.1 electrons) are in the methylene region and near C_{25} but again are not at chemically reasonable locations. Placement of half-atoms at pairs of locations with normal bond distances failed to refine to a reasonable model. The following equations of planes were calculated: for $\text{C}_1\text{-C}_6$, $-0.476X + 0.859Y - 0.188Z = 0.510$; for $\text{C}_7\text{-C}_{12}$, $-0.0876X + 0.959Y - 0.271Z = 1.436$; for $\text{C}_1, \text{C}_6\text{-C}_8$, $-0.289X + 0.926Y - 0.242Z = 1.305$.

Mass Spectral Data.

Mass spectral data were collected at 70eV and 15eV on an AEI MS-1201B mass spectrometer. Samples were introduced through the direct inlet at an ion source temperature of $125\text{-}150^\circ$ for compounds Ia, IIa,b and at 75° for Ib.

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