The Molecular Structure of 6, 8, 6 and Related Systems

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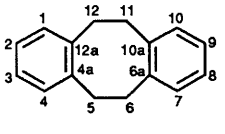
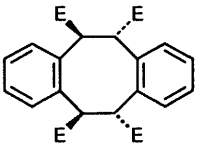
The crystal structures of 1,2;5,6-dibenzoocta-1,5-diene (**1**) ($C_{16}H_{16}$, $P2_1/n$ A = 6.638, B = 6.892, C = 12.625 Å, α = 90.00°, β = 96.58°, γ = 90.00°, Z = 2); 6,7,13,14-tetrahydrodipyrido[1,2-*a*:1,2-*e*]diazocinium dibromide (**11**) ($C_{14}H_{16}N_2Br_2{\cdot}2H_2O$, $P2_1/n$, A = 14.586, B = 6.146, C = 9.159 Å, α = 90.00°, β = 104.16°, γ = 90.00°, Z = 2); 1,2;5,6;9,10-tribenzododeca-1,5,9-triene (**12**) ($C_{24}H_{24}$, $P2_1/n$, A = 19.140, B = 5.122, C = 19.214 Å, α = 90.00°, β = 107.12°, γ = 90.00°, Z = 4) and 1,2;5,6;9,10;13,14-tetrabenzohexadeca-1,5,9,13-tetraene (**16**) ($C_{32}H_{32}$, $P2_1$, A = 12.560, B = 33.665, C = 11.312 Å, α = 90.00°, β = 90.38°, γ = 90.00°, Z = 8) have been determined. The first two, which belong to the 6,8,6 ring system, exist in the solid state in the chair conformation, whereas both the chair and the boat forms are present in solution. The central twelve-membered ring of compound **12** exists in the crystal as an almost perfect C_2 propeller, which is also the only observed conformation in solution. Finally, there are four different molecules of compound **16** in the crystal; however, they roughly correspond to the same conformation (and its enantiomer) [(+−+,−+−,++−,−−−) and (−+−,+−+, −−+,+++)]. Partial and complementary to literature NMR (^{1}H and ^{13}C) results agree with previous conformational analyses in solution.

The problem of the molecular structure of the so-called 6,8,6 ring systems, where 6 represents a six-membered aromatic compound, although important, remains practically unexplored. An examination of the literature, both through *Chemical Abstracts* and the CSD,[1] reveals that the simplest representative of this family, 1,2,5,6-dibenzoocta-1,5-diene (**1**), was studied in 1945 but in an incomplete way (see the following discussion).[2] The X-ray structures of three derivatives of the parent compound have been reported, **2**,[3] **3**[4] and **4**.[5]



1



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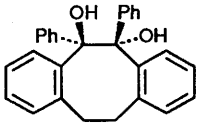

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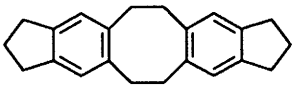

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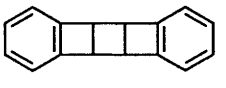
Related to **1** are the compounds in which the central cyclooctadiene ring has been modified. The structures of four compounds containing only carbon atoms have been described, **5**,[6] **6**,[7] **7**,[8] and **8**.[9]

Another, much more common modification, is to introduce heteroatoms in the central ring. All reported structures have the heteroatoms at positions 5, 6, 11 and/or 12.[9,10] All these compounds have been the subject of careful conformational analyses in solution.[11–14] Considering that related 5,8,5 heterocyclic derivatives **9**[15] and **10**[16] have been described, it is surprising that the structure of the 6,7,13,14-tetrahydrodipyrido[1,2-*a*:1,2-*e*]diazocinium cation (**11**) has never been published.

It was thus decided to determine the structure of compounds **1** and **11**. In the preparation of **1** from α,α′-dibromo-*o*-xylene,



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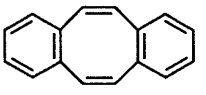

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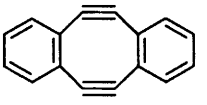

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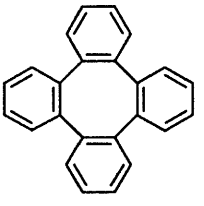

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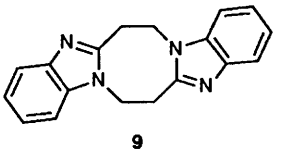

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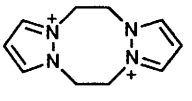

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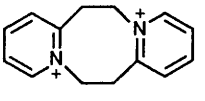
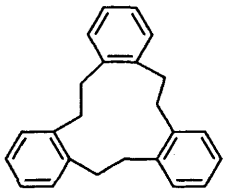


11

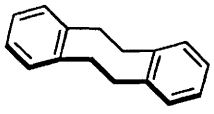
a trimer, 1,2;5,6;9,10-tribenzododeca-1,5,9-triene (**12**), is also formed.[2,12,17]

It is necessary to examine in more detail the seminal work of Baker, Banks, Lyon and Mann.[2] Using molecular models and the scarce crystallographic data available, they discussed the molecular structure of **1** and **12**. For **1**, Dr. E. M. Davidson determined the unit cell dimensions (a = 6.80, b = 6.84, c = 13.63 Å, β = 100°), the space group (monoclinic, $P2_1/c$) and the experimental density (0.986 g cm^{-3}). She concluded that the

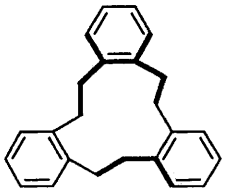


12

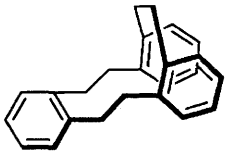
molecule has a centre of symmetry, a conclusion which is only consistent with the 'chair' conformation (**1c**) (for a discussion of the conformational behaviour of **1** in solution, see references [11,18–20]).



1c



12c



12h

In the case of compound **12**, Dr. M. Perutz determined that the crystals (needle-shaped with strong negative birefringence) are either orthorhombic or monoclinic. He concluded that of the four possible conformations proposed by Baker *et al.*,[2] only the propeller structure (**12c**) and the helical structure (**12h**) were consistent with the crystallographic data (for an NMR study of the conformation of this ring, see ref. 12).

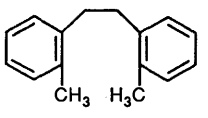
The crystallographic results reported above, although incomplete, were of such relevance that they have been quoted frequently (24 times between 1974 and 1991). The conformations of related compounds will be discussed in detail later on; but for the moment they can be classified as planar, compound **7**, chair (some authors call it *anti*), compounds **3**, **4**, **5**, **9** and **10**, and boat (also called tub), compounds **2**, **6** and **8**.

Results

Synthesis.—Compound **11**, a dibromide, was prepared by dimerization of 2-(β-bromoethyl)pyridine, according to Boekelheide and Feely.[21] Compound **1** has been described several times. Baker *et al.*[2] obtained it by treating α,α′-dibromo-*o*-xylene with sodium, and obtained 6% of **1** and a much smaller yield of **12**. Using the same reaction, Cope and Fenton,[17] after optimizing the procedure, obtained up to 46% of **1** accompanied by small amounts of **12** and 1,2-di(*o*-tolyl)ethane **13**. Müller and Röscheisen[22] increased the yield of **12** up to 35%, maintaining the yield of **1** at 40%. Compound **1** can also be obtained (40%) from xylene dianion and 1,2-dibromoethane.[23]

Actually, the Wurtz reaction between α,α′-dibromo-*o*-xylene and sodium is rather complex (see the discussion by Ollis and Stoddart).[12] Depending on the experimental conditions, either cyclic compounds **1** and **12** or acyclic hydrocarbons **13**,[2,12] **14**,[12] and **15**[12] were found.

In our hands, the reaction proved even more complex. Working in pure dioxane as solvent (see Experimental section),



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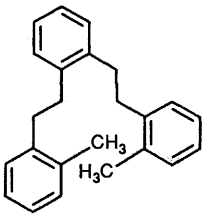

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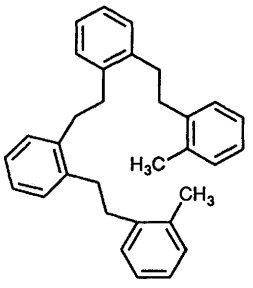

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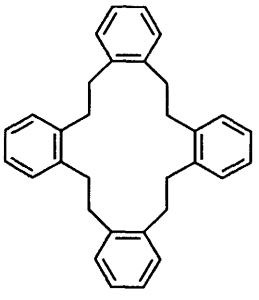
a mixture of cyclic compounds, including **1**, **12**, **16**, **17**, **18** and **19** was isolated (Table 1).

The R_f values vary smoothly with the ring size. Thus, using a mixture of hexane–diethyl ether (10:0.2), the R_f values follow the relationship $R_f = 1.336–0.441\sqrt{n}$, $r^2 = 0.997$ (n is the number of $C_6H_4CH_2CH_2$ units). For $n = 8$, the equation predicts $R_f = 0.09$, which is compatible with the existence of this macrocycle in the last fraction. Only for $n = 2$, 3 and 4, were the compounds isolated in sufficient amounts to obtain suitable crystals by repeated crystallisation.



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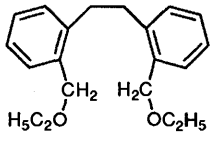
If the reaction is carried out in toluene, then *o*-xylene, 1,2-di-*o*-tolylethane (**13**), 1,2-bis(*o*-methylphenethyl)benzene (**14**), 1,2-bis(*o*-ethoxymethylphenyl)ethane (**17**) and α,α′-diethoxy-*o*-xylene (**18**), were isolated.



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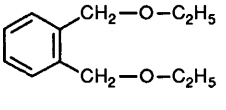

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Compounds **17** and **18** result from the diethyl ether used in the work-up procedure (see Experimental section).

Table 2 summarizes the results obtained with the four compounds, while Figs. 1–4 are different views (drawn with Pluto)[24] of these compounds and their packing modes. Free areas and free volumes were calculated according to Gavezzotti.[25]

1,2;5,6-*Dibenzoocta*-1,5-*diene* (**1**) *and Tetrahydrodipyrido-*

Table 1 Cyclic compounds obtained in the Wurtz reaction between α,α′-dibromo-*o*-xylene and sodium

Compound	Formula		*M*	M.p./°C	Lit. m.p./°C	Yield (%)	MS, $M^{\cdot+}$	R_f[a] A	B	C
1	$(C_6H_4CH_2CH_2)_2$	$C_{16}H_{16}$	208.30	109–110	110–112[22]	62.0	208.13	0.49	0.71	0.42
12	$(C_6H_4CH_2CH_2)_3$	$C_{24}H_{24}$	312.45	188.5–189	184–185[22]	30.0	312.22	0.43	0.59	0.34
16	$(C_6H_4CH_2CH_2)_4$	$C_{32}H_{32}$	416.61	198–201		5.0	416.20	0.40	0.44	0.25
17	$(C_6H_4CH_2CH_2)_5$	$C_{40}H_{40}$	520.76	204–206		0.8	520.62	0.33	0.35	0.17
18	$(C_6H_4CH_2CH_2)_6$	$C_{48}H_{48}$	624.91			0.4	624.79	0.29	0.25	0.12
19	$(C_6H_4CH_2CH_2)_7$	$C_{56}H_{56}$	729.06			< 0.4	729.00	0.24	0.18	<0.1
	$(C_6H_4CH_2CH_2)_8$	$C_{64}H_{64}$	833.21			1.4		0.18	0.10	<0.1

[a] A, hexane–benzene (10:6.5); B, hexane–diethyl ether (10:0.2); C, hexane–ethyl acetate (10:0.2).

Table 2 Crystallographic data for compounds **1**, **11**, **12** and **16**

	1	**11**	**12**	**16**
Formula	$C_{16}H_{16}$	$C_{14}H_{16}N_2Br_2{\cdot}2H_2O$	$C_{24}H_{24}$	$C_{32}H_{32}$
Molecular mass	208.30	406.12	312.45	416.60
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1$
A/Å	6.638(1)	14.586(3)	19.140(3)	12.560(2)
B/Å	6.892(1)	6.146(1)	5.122(1)	33.665(4)
C/Å	12.625(2)	9.159(2)	19.214(3)	11.312(2)
α/°	90.00	90.00	90.00	90.00
β/°	96.58(1)	104.16(1)	107.12(2)	90.38(1)
γ/°	90.00	90.00	90.00	90.00
Z	2	2	4	8
D_c/g cm^{-3}	1.206	1.701	1.151	1.159
V/Å^3	573.8(2)	796.1(4)	1800.2(6)	4783.0(13)
F(000)	224	408	672	1792
λCu/Å	1.541 78	1.541 78	1.541 78	1.541 78
μ/cm^{-1}	4.73	65.49	4.52	4.55
Absorption	no	yes	no	yes
Crystallization from	ethanol methanol	H_2O ethanol	acetone ethanol–hexane	benzene
No. of reflections	924	1375	2304	6173
No. of parameters	78	128	232	302–313
N_{rif}/N_{par}	11.8	10.7	10.0	20.1
R	0.0574	0.0490	0.0589	0.0679
R_w	0.0823	0.0592	0.0710	0.0714
Free area/Å^2	141.48	219.63	352.05	1651.27[a]
Free volume/Å^3	118.87	158.76	537.72	1741.85[a]
Molecular volume/Å^3	113.73	159.34	315.62	1520.56[a]
Packing coefficient	0.793	0.801	0.701	0.636[a]

[a] These values refer to calculation performed with the contributions of only 32 carbon atoms of the $C_{32}H_{32}$ compound, because the dimensions of program OPEC did not permit the introduction of more than 128 atoms, so that the 32 hydrogens of the four independent molecules have been discarded.

[1,2-a:1,2-e]*diazocinium Dibromide* (**11**).—Bond distances and angles are in the range usually reported for this class of compound.[1] For instance, bond angles in the bridges are wider than standard sp^3 angles, but this is a general feature of cyclophanes.[5] The six-membered ring forms an angle of 0.86° with the plane through C(**1**)–C(2)–C(7)–C(8) in **1**, and angle of 0.63° with the plane N(1)–C(2)–C(7)–C(8) in **11**, whereas the angle the same six-membered rings make with the plane constructed with the C(7)–C(8) atoms and the corresponding centrosymmetric C(7′)–C(8′) are 61.49° and 62.98°, respectively, in the same compounds. The Br atom is 3.446 Å distant from the plane N(1)···C(6) in **11** as in the bis(pyrazolo)tetrazocinium dibromide (**10**).[16] Both structures have a chair conformation, their sideviews [Fig. 1(*b*) and 2(*b*)] being perfectly superimposable, confirming the hypothesis made in the late work of Baker (note small differences with regard to Davidson's work in the space group, cell dimensions and density).[2]

Concerning the packing of compound **1**, there are no carbon–carbon intermolecular distances less than 3.5 Å and the closest carbon–hydrogen intermolecular distance is 2.83 Å. That of the salt **11** is more interesting. Owing to the presence of the water molecule and the bromine ion, possible hydrogen bonds are given in Table 3.

1,2;5,6;9,10-*Tribenzododeca*-1,5,9-*triene* (**12**).—Compound $C_{24}H_{24}$ shows two rings quite parallel [Figs. 3(*a*) and (*b*)], the angle between them being 3.71°, while the third one makes quite similar angles with the other two (19.1 and 21.7°, respectively); in this way the molecule assumes the conformation **12c** corresponding to the so-called propeller structure. Here again, the expectation based on Perutz's report and the results of molecular models was verified; of the possible conformations the asymmetric one, C_2, is present in the solid state.

Concerning the packing of this molecule, the minimum intermolecular distances are C(3)–C(12) = 3.500 Å and C(24)–H(23) = 2.774 Å.

1,2;5,6;9,10;13,14-*Tetrabenzohexadeca*-1,5,9,13-*tetraene* **16**.—In $C_{32}H_{32}$ the space group is non-centrosymmetric

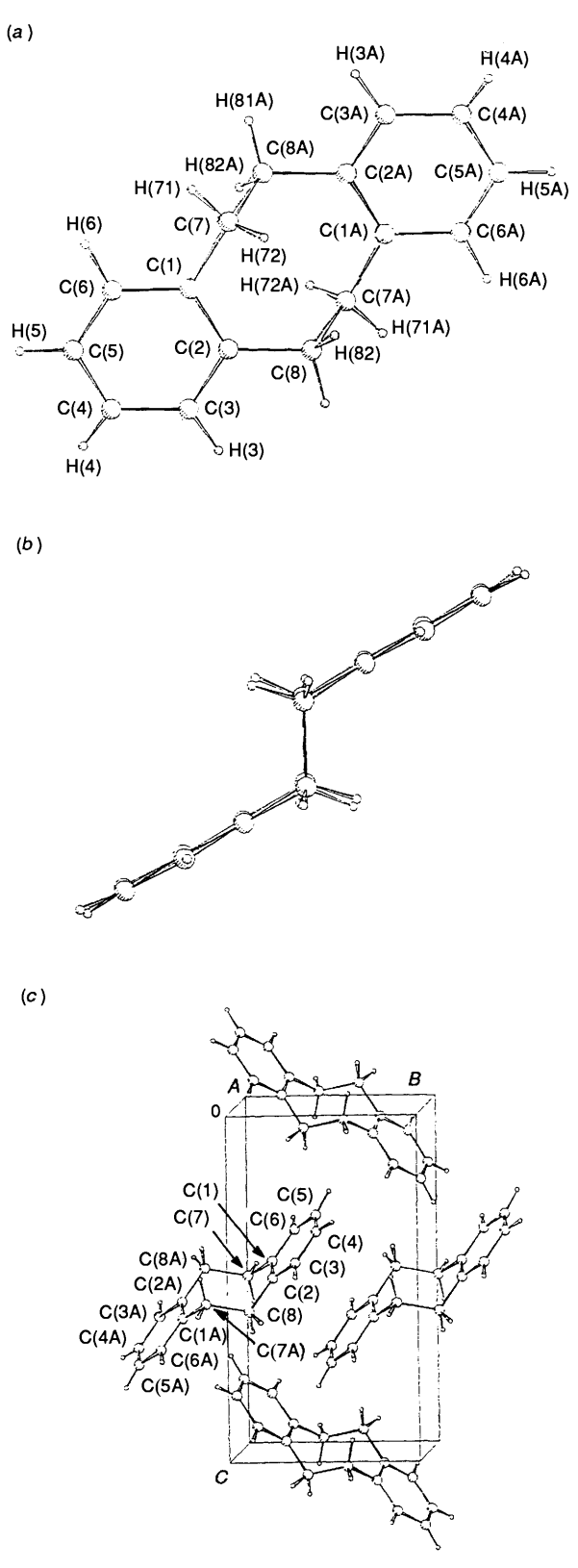


Fig. 1 (*a*) Perspective view of compound 1 ($C_{16}H_{16}$) with the atomic numbering scheme used; (*b*) sideview of molecule 1; (*c*) packing diagram of compound **1** with unit cell outlines

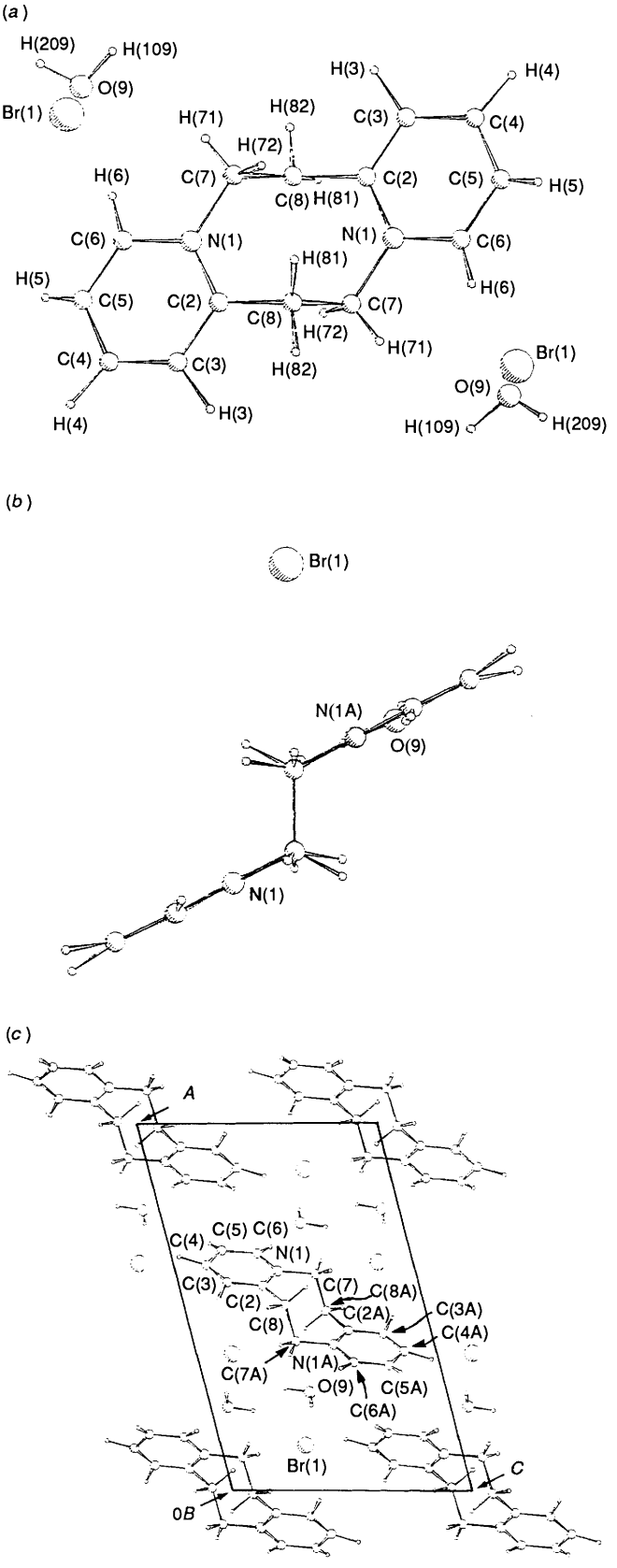


Fig. 2 (*a*) Perspective view of compound 11 ($C_{14}H_{16}N_2Br_2{\cdot}2H_2O$) with atomic labelling; (*b*) sideview of molecule **11**; (*c*) projection along the *b* axis of the atomic arrangement of the molecule **11**

whereas for the previous three compounds it was centric. This compound has been solved in space group $P2_1$ with four independent molecules [Figs. 4(*a*)–(*d*)] in the unit cell. The relevant torsional angles for the central sixteen-membered ring are collected in Table 4.

Two by two (**1** and B, on one hand, and A and C, on the other) these molecules are nearly superimposable by a combination of a translation and a rotation. Furthermore, the averaged

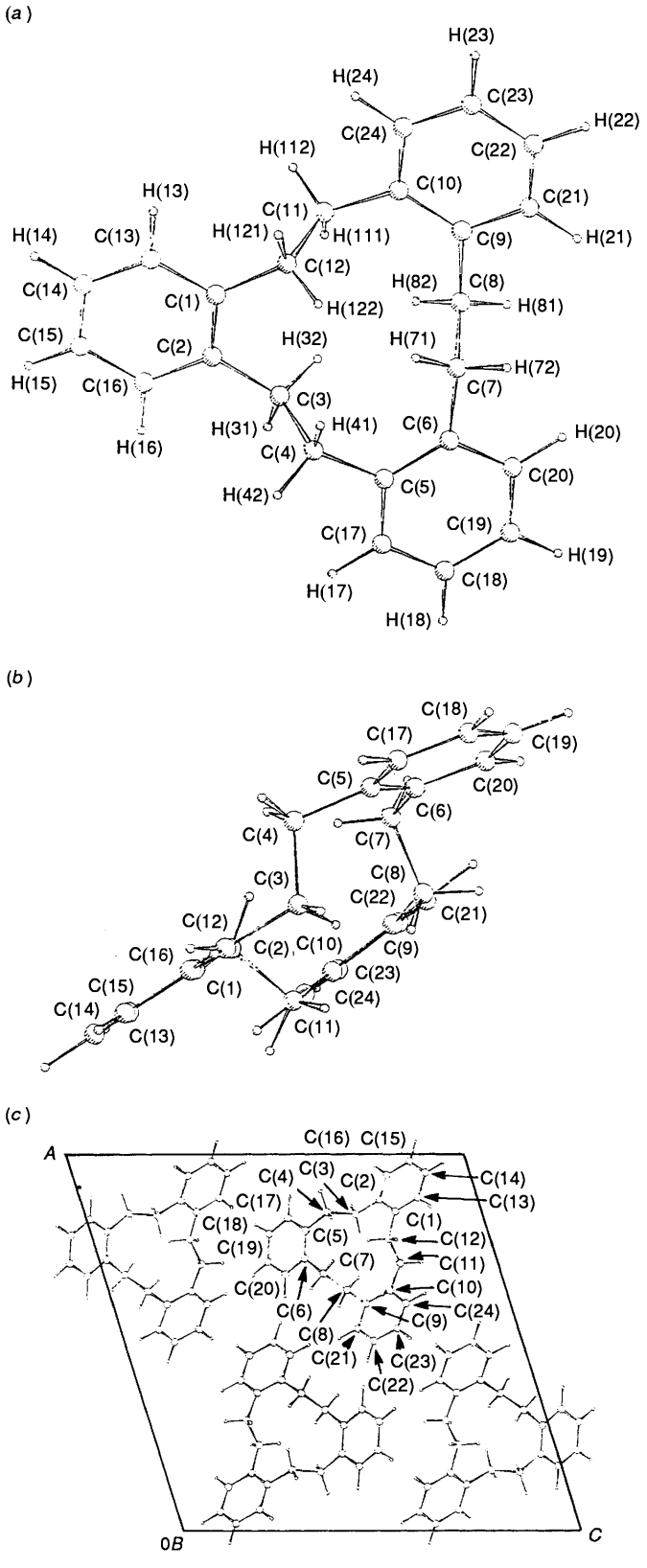


Fig. 3 (*a*) Molecular structure of compound **12** ($C_{24}H_{24}$) viewed from the direction giving the minimum overlap, with the atomic numbering scheme used; (*b*) sideview of molecule **12**; (*c*) perspective view of the contents of the unit cell of compound **12** along the *b* axis

values for **1**/B and A/C pairs are very close but for the sign. Since two conformations with the same angles and opposite signs correspond to a pair of enantiomers,[11,12,19] we can conclude that only one conformation (150.2,−172.9,88.3; − 105.1,171.8, −172.5; 83.7,64.8,−104.0; −92.8,−162.4,−94.8) and its enantiomer is present in the solid state. Nevertheless, in this very flexible ring system, the aforementioned conformation is not simply related to a conformation of high symmetry.

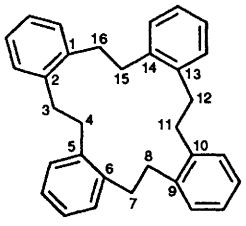
As regards the packing of this compound, owing to the great number of atoms (128 C and 128 H) the calculation of all intermolecular contacts is beyond the capabilities of the PARST program (maximum number of atoms = 200). Calculations performed with only 128 carbon atoms show that here also there are no intermolecular contacts of less than 3.5 Å, the shortest one being 3.568 Å.

Table 3 Some significant distances and angles pertaining to be hydrogen bonding in salt **11**

	Distance/Å	Angle/°
C(6)···O(9)[a]	3.340(6)	
O(9)···Br[b]	3.351(4)	
O(9)···Br[c]	3.353(4)	
C(6)···H(6)	1.08(4)	
O(9)···H(1)O(9)	1.07(10)	
O(9)···H(2)O(9)	0.94(7)	
H(6)···O(9)[a]	2.278(6)	
H(1)O(9)···Br[b]	2.329(11)	
H(2)O(9)···Br[c]	2.561(8)	
C(6)–H(6)···O(9)[a]		167.1(4)
O(9)–H(1)O(9)···Br[b]		159.5(6.9)
O(9)–H(2)O(9)···Br[c]		169.4(6.9)

[a] Symmetry operator, $-x+1, -y, -z+1$. [b] Symmetry operator $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$. [c] Symmetry operator $x, y+1, z$.

Table 4 Dihedral angles of the central sixteen-membered ring for the four independent molecules of compound $C_{32}H_{32}$ (**16**)



	Molecule			
Dihedral angle	1	A	B	C
C(1)–C(2)–C(3)–C(4)	153.54	−151.98	146.31	−148.99
C(2)–C(3)–C(4)–C(5)	−172.93	170.58	−174.19	173.78
C(3)–C(4)–C(5)–C(6)	89.64	−86.38	88.72	−88.33
C(5)–C(6)–C(7)–C(8)	−102.20	101.82	−106.50	110.07
C(6)–C(7)–C(8)–C(9)	173.97	−174.39	168.92	−169.89
C(7)–C(8)–C(9)–C(10)	−173.82	173.84	−173.37	168.88
C(9)–C(10)–C(11)–C(12)	81.52	−84.22	83.58	−85.55
C(10)–C(11)–C(12)–C(13)	67.13	−62.52	66.06	−63.74
C(11)–C(12)–C(13)–C(14)	−108.85	102.01	−101.70	103.52
C(13)–C(14)–C(15)–C(16)	−92.51	88.43	−93.46	97.06
C(14)–C(15)–C(16)–C(1)	−163.89	163.71	−160.71	161.47
C(15)–C(16)–C(1)–C(2)	−97.69	100.63	−99.34	95.93

NMR Spectroscopy.—Since ^1H and ^{13}C NMR spectroscopy have already been used for studying the thermodynamic and kinetic aspects of the conformation of rings **1** and **12**, our contribution will be only complementary. A brief summary of the literature results is reported in Table 5.

The main difference between structures **12c** and **12d** is that the former should present two identical ABCDs and one AA′BB′ system, for both phenyl rings and ethanes, whereas the latter should present three identical AA′BB′ for phenyls and for

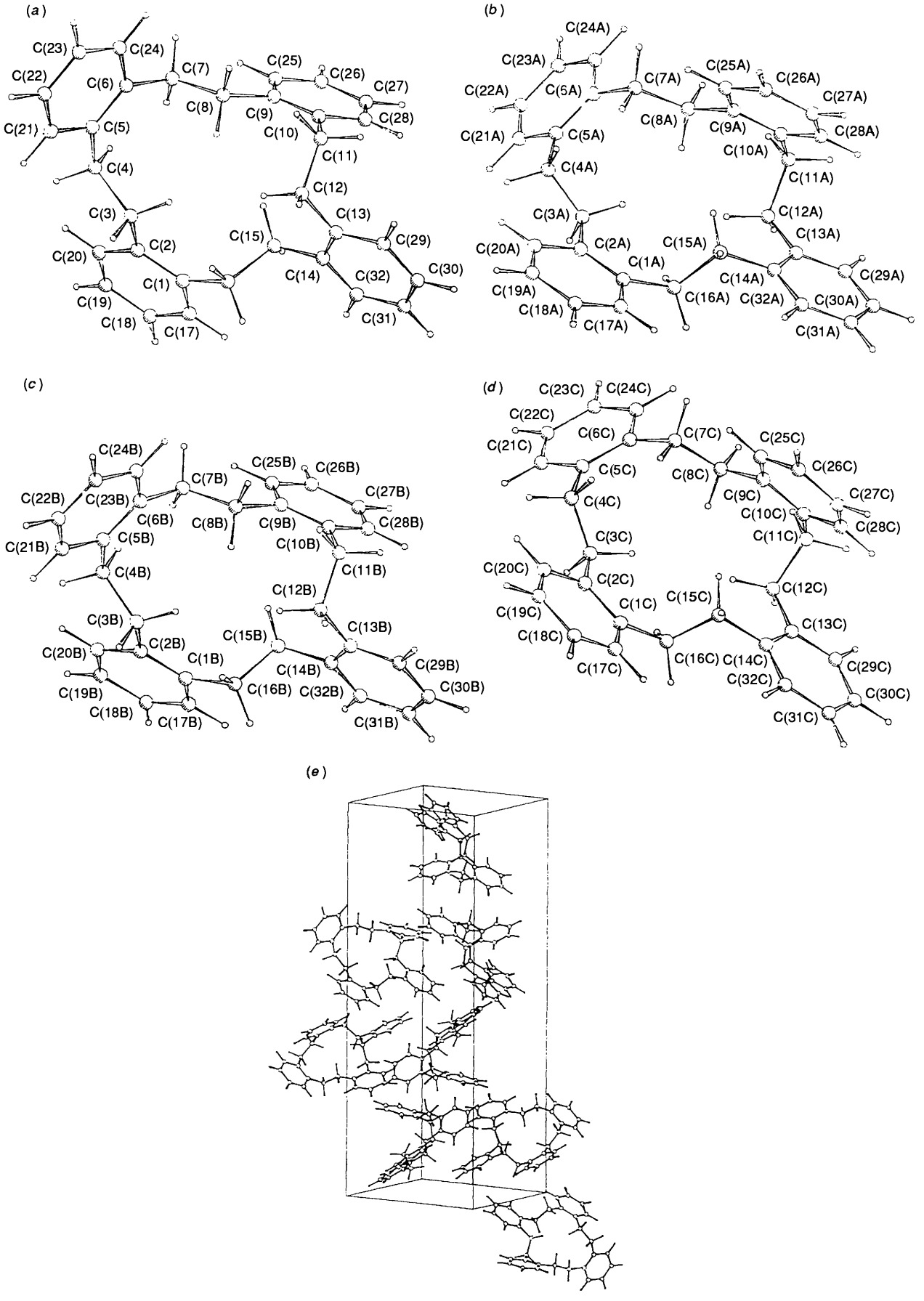
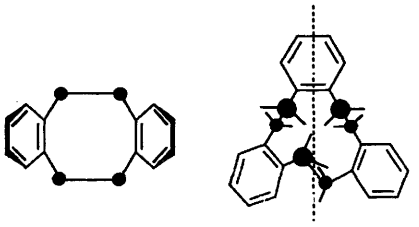


Fig. 4 Best perspective view of the independent molecule 1 of compound **16** ($C_{32}H_{32}$) with the atomic numbering scheme used; (*b*) best perspective view of the independent molecule **A** of compound **16** with the atomic numbering scheme used; (*c*) best perspective view of the independent molecule **B** of compound **16** with the atomic numbering scheme used; (*d*) best perspective view of the independent molecule **C** of compound **16** with the atomic numbering scheme used; (*e*) perspective view of the unit cell of compound **16**.

Table 5 Literature results on compounds 1 and **2**



$C_2(-\pi/2-, +\pi/2+, -\pi/2-)$ $D_2(+\pi/2+, +\pi/2+, +\pi/2+)$

1b **12c** **12d**

Compound	Thermodynamic	Kinetic
1[20]	In $CDCl_3$–CS_2 (2:3) at 183 K a mixture of 60% **1b**–40% **1c** In CD_2Cl_2–C_3H_6 (2:1) at 147 K 80% **1b**–20% **1c**	**1b** ⇌ **1c** $\Delta G^{\ddagger}$ 10.0 kcal mol^{-1} **1b** ⇌ **1b** $\Delta G^{\ddagger}$ 7.8 kcal mol^{-1}
12[19]	Only the propeller structure **12c**	**12c** ⇌ **12c** $\Delta G^{\ddagger}$ 10.0 kcal mol^{-1}

Table 6 ^{1}H NMR data (δ in ppm, J in Hz) of compounds **1**, **11**, **12** and **16**

Compound	Solvent	T/K	^{1}H NMR data
1	$CDCl_3$[a]	298	CH_2: 3.06(s); C_6H_4: AA′BB′, δ_A = 6.98, δ_B = 7.00 J_{AB} = 7.32, $J_{AB'}$ = 1.22, $J_{AA'}$ = 0.46, $J_{BB'}$ = 7.44
11	$[^2H_6]Me_2SO$[a]	353	CH_2(5): 4.07, CH_2(6): 5.24,[b] J_{AB} = 6.4; 9.14(H_1), 8.06 (H_2,H_3), 8.52(H_4),[b] J_{12} = 5.8, J_{34} = 7.5
	$CDCl_3$[a]	298	CH_2: 3.03(s); C_6H_4: AA′BB′, δ_A = 7.22, δ_B = 7.32 J_{AB} = 7.43, $J_{AB'}$ = 1.29, $J_{AA'}$ = 7.42, $J_{BB'}$ = 0.42
12	CD_2Cl_2 + CS_2 (2:1)[a]	170	CH_2CH_2: AA′BB′ + $[ABCD]_2$ AA′BB′, δ_A = $\delta_{A'}$ = 2.92, δ_B = $\delta_{B'}$ = 3.12, $J_{gem} \approx -13$, $J_{gauche} \approx 7$, $J_{trans} \approx 13$ ABCD, δ_A = 2.72, δ_B = 2.74, δ_C = 3.17, δ_D = 3.29, $J_{gem} \approx -13$, $J_{gauche} \approx 3$, $J_{trans} \approx 14$ C_6H_4: $[ABCD]_2$ + AA′BB′, 7.17–7.28 (m, 10 H), 7.37 (d, 2 H, J_0 = 7.0)
16	$CDCl_3$[a]	298	CH_2: 2.89(s), C_6H_4: AA′BB′, δ_A = 7.14, δ_B = 7.24
o-Xylene	$CDCl_3$	298	CH_3: 2.24; C_6H_4: AA′BB′, δ_A = 7.08, δ_B = 7.11 (broadened due to coupling with the CH_3)

[a] 500 MHz; [b] very broad at 298 K.

Table 7 ^{13}C NMR data (δ in ppm, ^{1}H–^{13}C coupling constants in Hz) of compounds 1, **11**, **12** and **16**

Compound	Solvent	T/K	C_1	C_2	C_3	C_4	C_{4a}	C_5	C_6
1	$CDCl_3$	298	129.6 ^1J = 157.9	126.1 ^1J = 159.4 ^3J = 6.7			140.5	35.1 ^1J = 128.9	
1c −35% **1b** −65%	$[^2H_6]$Acetone	168	130.6 130.6	127.1 127.1			139.5 143.9	37.2 35.4	
11	$[^2H_6]Me_2SO$	313	147.6 ^1J = 190.5	128.6 ^1J = 176.0	148.0 ^1J = 171.1	132.1 ^1J = 177.3	153.7[a]	56.4[a]	34.2 ^1J = 133.9
12	$CDCl_3$	298	130.4 ^1J = 156.8	126.7 ^1J = 160.0 ^3J = 7.7			140.0	37.3 ^1J = 129.1	
16	$CDCl_3$	298	128.7 ^1J = 157.5	126.3 ^1J = 159.8 ^3J = 7.2			139.5	33.3 ^1J = 130.2	
o-Xylene	$CDCl_3$	298	129.5 ^{1}J = 157.0 ^2J = 4.6 ^3J = 4.6 ^4J = 1.9 (CH_3)	125.8 ^1J = 159.7 ^3J = 6.5			136.4	19.7 ^1J = 125.6	

[a] Broad Signals at 298 K.

Table 8 Conformation of the central ring in 6,8,6 systems in the solid state

Compound	Torsion angles/°	Conformation	Averaged values/°
1 Chair[25] (C)	74.5, −109.3, 74.5 −74.5, 109.3, −74.5	C	74.5, −109.3, 74.5
1 Twist-boat[25] (TB)	89.1, −26.5, −53.9 −53.9, −26.5, −89.1	TB	89.1, −26.5, −53.9
1 Boat[25] (B)	74.3, 0, −74.3 −74.3, 0, 74.3	B	74.3, 0, −74.3
1 (This work)	74, 109, 73 −73, 109, −74	C	73.3, −109, 73.5
2[3]	74, −8, −67 93, −37, −44	TB	84, −22, −56
3[4]	73, −100, 70 −72, 110, −76	C	73, −105, 73
4[5]	74, −110, 73 −73, 110, −74	C	73.4, −110, 73.4
9[15]	69, −101, 74 −74, 101, −69	C	72, −101, 72
10[16]	72, −105, 75 −75, 105, −72	C	73, −105, 73
11 (This work)	74, −113, 76 −74, 113, −76	C	75, −113, 75

ethane fragments. Otherwise, the systems are quite similar, for instance, the ethane fragments are always in the staggered conformation (Ar–C–C–Ar dihedral angle near $\pi/2$). Our results are summarized in Tables 6 (^{1}H NMR data) and 7 (^{13}C NMR data).

The aromatic AA′BB′ systems have been analysed and assigned using the small coupling between *ortho* protons [H(1), H(4), H(7), H(10)] and the CH_2 protons. This coupling is also present in *o*-xylene; for this compound the protons of Table 6 and the carbons of Table 7 (assigned according to Kalinowski),[26] have been connected through a 2D (^{1}H–^{13}C) correlated spectrum.

The complete analysis of the ^{1}H NMR spectrum of **12** at 170 K is very complex, even at 500 MHz, owing to couplings between the aromatic *ortho* protons and the methylene protons and also between the methylene protons of different ethane fragments.[27] Nevertheless, it clearly shows two identical ethane groups in the form of an ABCD system and the third one as a quasi degenerate AA′BB′ system, both with staggered-like coupling constants (conformation **12c**, Table 5). The ^{13}C NMR spectrum of compound **1** (Table 7) has not previously been reported. Finally, the dipyridodiazocinium dibromide (**11**) shows in NMR spectroscopy a dynamic behaviour which considerably enlarges some signals; however, its low solubility in common solvents and its low stability, prevents further studies. Subsequently, for compound **12** a chair–chair interconversion is very unlikely, the broadening probably involving boat or twist-boat forms.

Discussion

The 6,8,6 systems crystallize preferably in the chair conformation, compound **2** being the only exception. In Table 8 there is a summary of all available information.

It is noteworthy how accurate Allinger's calculations were, using his well-known force-field method.[28] The dibenzooctadiene **1** is an almost perfect chair (**1c**) in agreement with Davidson's inference. The twist-boat conformation of compound **2** in the Allinger sense corresponds to a situation intermediate between the boat (−0+ −0+) and the transition state FB1 (0− +0− +) according to Ollis' definition.[19]

The twelve-membered ring of compound **12** in the solid state also has a conformation consistent with one of Perutz's hypothesis and, in this case, coincident with the conformation present in solution (Table 5). It is an almost perfect C_2 propeller, which, according to Ollis' notation (− + −,+ − +,+ − +) [in fact, it can be better described as ($-\pi/2-$,$+\pi/2+$,$+\pi/2+$), since the central Ar–C–C–Ar bond has an almost 180° dihedral angle] can be described as (−103.63,+175.53,−93.28; +88.93,−173.12,+84.55; +82.56,−173.79,+80.49). Simple mechanical calculations performed with the DTMM program,[29] show that **12c** is indeed the minimum energy conformation (−23.93 kJ mol^{-1}). Other conformations such as D_3 (**12d**, see Table 5) and those described by Ollis *et al.*[12] such as C_s (+8.86 kJ mol^{-1}), C_{3v} (+25.70 kJ mol^{-1}) and C_{3h} (+59.12 kJ mol^{-1}) are much higher in the energy scale.

Finally, the sixteen-membered central ring of compound **16** is too flexible to be studied by DNMR spectroscopy (nothing is observed at 200 MHz at temperatures as low as 170 K). Views of the conformation present in the solid state are represented in Figs. 4(*a*)–(*d*) and the packing in Fig. 4(*e*).

Experimental

Chemistry.—Melting points were recorded on a Büchi 530 apparatus and are uncorrected. Mass spectra were carried out on VG-12-250 at 70 eV, Hewlett–Packard GC/MS 5985 and LC/MS 5988A (interface *HP1090 LC*) spectrometers. The detection mode for the Hewlett–Packard spectrometers was the flow injection particle beam interface. When chemical

Table 9 Atomic coordinates for compounds 1, 11, 12 and 16

Atom	*x*/*A*	*y*/*B*	*z*/*C*	Atom	*x*/*A*	*y*/*B*	*z*/*C*
1							
C(1)	0.065 50(14)	0.227 65(17)	0.421 24(10)	C(7)	0.223 91(24)	0.086 63(25)	0.470 93(14)
C(2)	−0.122 07(14)	0.24 848(17)	0.459 75(10)	C(8)	−0.176 24(27)	0.130 28(25)	0.553 91(13)
C(3)	−0.264 98(14)	0.378 08(17)	0.410 74(10)	C(1A)	−0.065 50(14)	−0.227 65(17)	0.578 76(10)
C(4)	−0.220 31(14)	0.486 85(17)	0.323 21(10)	C(2A)	0.122 07(14)	−0.248 48(17)	0.540 25(10)
C(5)	−0.032 74(14)	0.466 02(17)	0.284 70(10)	C(7A)	−0.223 91(24)	−0.086 63(25)	0.529 07(14)
C(6)	0.110 17(14)	0.336 42(17)	0.333 72(10)	C(8A)	0.176 24(27)	−0.130 28(25)	0.446 09(13)
11							
Br(1)	0.124 57(3)	0.120 07(7)	0.353 70(5)	C(7)	0.591 65(25)	−0.152 81(69)	0.577 80(47)
N(1)	0.600 86(22)	−0.111 89(45)	0.422 39(40)	C(8)	0.508 49(23)	0.227 99(57)	0.417 62(44)
C(2)	0.561 68(24)	0.070 13(61)	0.344 96(41)	O(9)	0.269 26(24)	0.688 81(72)	0.428 75(44)
C(3)	0.571 85(30)	0.103 61(65)	0.202 11(49)	N(1A)	0.399 14(22)	0.111 89(45)	0.577 61(40)
C(4)	0.619 44(30)	−0.045 08(88)	0.134 40(47)	C(2A)	0.438 32(24)	−0.070 13(61)	0.655 04(41)
C(5)	0.657 78(27)	−0.227 83(79)	0.212 33(49)	C(7A)	0.408 35(25)	0.152 81(69)	0.422 20(47)
C(6)	0.649 19(26)	−0.257 01(70)	0.357 44(46)	C(8A)	0.491 51(23)	−0.227 99(57)	0.582 38(44)
12							
C(1)	0.845 95(8)	0.265 09(31)	0.783 33(8)	C(13)	0.882 56(8)	0.360 91(31)	0.852 41(8)
C(2)	0.876 80(8)	0.064 27(31)	0.753 09(8)	C(14)	0.950 02(8)	0.255 92(31)	0.891 25(8)
C(3)	0.838 10(13)	−0.057 65(47)	0.679 95(12)	C(15)	0.980 87(8)	0.055 11(31)	0.861 01(8)
C(4)	0.843 57(13)	0.084 71(50)	0.611 29(13)	C(16)	0.944 26(8)	−0.040 72(31)	0.791 93(8)
C(5)	0.795 13(6)	−0.046 65(34)	0.542 92(8)	C(17)	0.827 85(6)	−0.229 58(34)	0.508 66(8)
C(6)	0.719 99(6)	−0.002 43(34)	0.517 07(8)	C(18)	0.785 42(6)	−0.368 28(34)	0.448 55(8)
C(7)	0.679 49(14)	0.189 28(51)	0.551 70(14)	C(19)	0.710 28(6)	−0.324 06(34)	0.422 69(8)
C(8)	0.635 81(15)	0.058 22(52)	0.597 63(15)	C(20)	0.677 56(6)	−0.141 13(34)	0.456 95(8)
C(9)	0.600 88(8)	0.256 15(36)	0.636 19(7)	C(21)	0.534 52(8)	0.364 36(36)	0.595 55(7)
C(10)	0.634 24(8)	0.342 59(36)	0.707 06(7)	C(22)	0.501 53(8)	0.559 00(36)	0.625 78(7)
C(11)	0.706 27(13)	0.233 87(51)	0.754 59(14)	C(23)	0.534 89(8)	0.645 43(36)	0.696 65(7)
C(12)	0.771 87(12)	0.383 28(46)	0.744 17(13)	C(24)	0.601 24(8)	0.537 22(36)	0.737 29(7)
16							
C(1)	0.686 35(25)	0.444 65(10)	−0.311 05(32)	C(12A)	0.937 75(44)	0.613 39(18)	0.097 34(55)
C(2)	0.767 43(25)	0.422 55(10)	−0.363 18(32)	C(13A)	0.838 11(32)	0.587 34(12)	0.095 76(26)
C(3)	0.842 79(43)	0.399 60(0)	−0.286 89(51)	C(14A)	0.792 48(32)	0.572 66(12)	−0.008 18(26)
C(4)	0.891 87(53)	0.362 46(19)	−0.353 27(55)	C(15A)	0.835 72(43)	0.581 87(17)	−0.131 71(47)
C(5)	0.959 44(30)	0.334 68(11)	−0.275 89(35)	C(16A)	0.922 53(43)	0.551 86(17)	−0.172 24(47)
C(6)	0.915 53(30)	0.302 57(11)	−0.215 38(35)	C(17A)	0.868 24(23)	0.533 16(10)	−0.374 54(33)
C(7)	0.797 00(48)	0.294 20(22)	−0.213 01(65)	C(18A)	0.880 47(23)	0.532 11(10)	−0.496 98(33)
C(8)	0.752 38(46)	0.308 00(22)	−0.093 94(60)	C(19A)	0.965 06(23)	0.552 16(10)	−0.549 53(33)
C(9)	0.630 46(33)	0.305 77(13)	−0.080 29(34)	C(20A)	1.037 43(23)	0.573 25(10)	−0.479 63(33)
C(10)	0.585 58(33)	0.321 62(13)	0.021 85(34)	C(21A)	1.328 55(31)	0.654 80(11)	−0.276 07(34)
C(11)	0.649 92(47)	0.341 57(20)	0.118 86(54)	C(22A)	1.396 37(31)	0.680 80(11)	−0.215 98(34)
C(12)	0.677 03(45)	0.384 70(18)	0.091 72(54)	C(23A)	1.354 60(31)	0.713 56(11)	−0.156 71(34)
C(13)	0.581 34(31)	0.411 65(12)	0.088 98(25)	C(24A)	1.245 02(31)	0.720 32(11)	−0.157 52(34)
C(14)	0.539 59(31)	0.428 26(12)	−0.014 36(25)	C(25A)	0.828 67(35)	0.707 59(13)	−0.171 58(33)
C(15)	0.580 14(44)	0.418 22(17)	−0.136 30(47)	C(26A)	0.718 32(35)	0.709 17(13)	−0.159 19(33)
C(16)	0.667 71(45)	0.447 18(17)	−0.177 55(48)	C(27A)	0.670 88(35)	0.694 58(13)	−0.056 84(33)
C(17)	0.616 56(25)	0.466 71(10)	−0.381 51(32)	C(28A)	0.733 79(35)	0.678 40(13)	0.033 13(33)
C(18)	0.627 85(25)	0.466 67(10)	−0.504 11(32)	C(29A)	0.794 18(32)	0.577 58(12)	0.204 92(26)
C(19)	0.708 92(25)	0.444 58(10)	−0.556 25(32)	C(30A)	0.704 62(32)	0.553 15(12)	0.210 14(26)
C(20)	0.778 71(25)	0.422 52(10)	−0.485 78(32)	C(31A)	0.659 00(32)	0.538 47(12)	0.106 21(26)
C(21)	1.069 20(30)	0.340 98(11)	−0.272 95(35)	C(32A)	0.702 93(32)	0.548 23(12)	−0.002 96(26)
C(22)	1.135 05(30)	0.315 18(11)	−0.209 51(35)	C(1B)	0.562 11(24)	0.052 34(11)	0.462 57(33)
C(23)	1.091 14(30)	0.283 07(11)	−0.14 899(35)	C(2B)	0.477 91(24)	0.072 19(11)	0.407 38(33)
C(24)	0.981 38(30)	0.276 77(11)	−0.151 93(35)	C(3B)	0.398 23(45)	0.096 29(18)	0.479 57(51)
C(25)	0.565 17(33)	0.289 31(13)	−0.167 68(34)	C(4B)	0.356 55(58)	0.133 06(20)	0.414 15(58)
C(26)	0.455 00(33)	0.288 69(13)	−0.152 92(34)	C(5B)	0.285 99(31)	0.159 61(11)	0.488 69(35)
C(27)	0.410 13(33)	0.304 54(13)	−0.050 77(34)	C(6B)	0.324 68(31)	0.190 43(11)	0.559 29(35)
C(28)	0.475 41(33)	0.321 00(13)	0.036 61(34)	C(7B)	0.441 12(50)	0.200 22(25)	0.565 30(65)
C(29)	0.535 74(31)	0.420 56(12)	0.197 93(25)	C(8B)	0.491 29(45)	0.187 83(23)	0.676 90(61)
C(30)	0.448 39(31)	0.446 07(12)	0.203 53(25)	C(9B)	0.614 37(31)	0.189 13(12)	0.684 89(28)
C(31)	0.406 64(31)	0.462 67(12)	0.100 18(25)	C(10B)	0.666 01(31)	0.173 79(12)	0.784 44(28)
C(32)	0.452 24(31)	0.453 76(12)	−0.008 77(25)	C(11B)	0.603 82(51)	0.156 80(19)	0.888 67(51)
C(1A)	0.940 61(23)	0.554 25(10)	−0.304 64(33)	C(12B)	0.569 91(43)	0.112 89(18)	0.870 29(54)
C(2A)	1.025 20(23)	0.574 30(10)	−0.357 19(33)	C(13B)	0.666 58(31)	0.085 02(12)	0.866 50(24)
C(3A)	1.105 79(48)	0.599 51(19)	−0.283 54(53)	C(14B)	0.707 25(31)	0.070 00(12)	0.761 10(24)
C(4A)	1.154 68(57)	0.632 87(20)	−0.350 87(56)	C(15B)	0.661 87(45)	0.080 37(17)	0.638 82(46)
C(5A)	1.218 97(31)	0.661 56(11)	−0.276 88(34)	C(16B)	0.579 35(45)	0.050 51(17)	0.595 90(47)
C(6A)	1.177 21(31)	0.694 32(11)	−0.217 60(34)	C(17B)	0.635 29(24)	0.031 17(11)	0.395 03(33)
C(7A)	1.056 28(48)	0.701 82(23)	−0.213 00(69)	C(18B)	0.624 28(24)	0.029 85(11)	0.272 30(33)
C(8A)	1.011 87(47)	0.689 57(23)	−0.096 58(59)	C(19B)	0.540 08(24)	0.049 70(11)	0.217 11(33)
C(9A)	0.891 58(35)	0.691 41(13)	−0.081 61(33)	C(20B)	0.466 89(24)	0.070 87(11)	0.284 65(33)
C(10A)	0.844 14(35)	0.676 82(13)	0.020 75(33)	C(21B)	0.176 61(31)	0.152 90(11)	0.479 98(35)
C(11A)	0.910 87(53)	0.658 38(20)	0.115 95(52)	C(22B)	0.105 93(31)	0.177 03(11)	0.541 86(35)

Table 9 (*continued*)

Atom	x/A	y/B	z/C	Atom	x/A	y/B	z/C
C(23B)	0.144 63(31)	0.207 86(11)	0.612 46(35)	C(12C)	0.169 34(46)	0.385 89(19)	0.141 18(58)
C(24B)	0.254 00(31)	0.214 56(11)	0.621 18(35)	C(13C)	0.074 60(32)	0.413 61(12)	0.148 25(26)
C(25B)	0.673 71(31)	0.203 32(12)	0.590 01(28)	C(14C)	0.036 54(32)	0.429 21(12)	0.254 12(26)
C(26B)	0.784 68(31)	0.202 16(12)	0.594 67(28)	C(15C)	0.082 30(48)	0.418 15(18)	0.375 66(47)
C(27B)	0.836 32(31)	0.186 82(21)	0.694 22(28)	C(16C)	0.164 38(42)	0.448 64(16)	0.421 44(48)
C(28B)	0.776 98(31)	0.172 63(12)	0.789 11(28)	C(17C)	0.110 01(24)	0.466 10(10)	0.625 06(32)
C(29B)	0.713 21(31)	0.074 43(12)	0.974 24(24)	C(18C)	0.120 12(24)	0.465 56(10)	0.747 93(32)
C(30B)	0.800 51(31)	0.048 82(12)	0.976 58(24)	C(19C)	0.202 29(24)	0.444 04(10)	0.801 28(32)
C(31B)	0.841 19(31)	0.033 80(12)	0.871 19(24)	C(20C)	0.274 35(24)	0.423 06(10)	0.731 76(32)
C(32B)	0.794 56(31)	0.04 439(12)	0.763 45(24)	C(21C)	0.564 95(31)	0.343 44(12)	0.525 81(36)
C(1C)	0.182 07(24)	0.445 12(10)	0.555 54(32)	C(22C)	0.634 20(31)	0.319 79(12)	0.460 42(36)
C(2C)	0.264 24(24)	0.423 60(10)	0.608 89(32)	C(23C)	0.593 82(31)	0.289 87(12)	0.387 55(36)
C(3C)	0.34 400(50)	0.399 97(20)	0.534 18(58)	C(24C)	0.484 20(31)	0.283 59(12)	0.380 07(36)
C(4C)	0.384 93(52)	0.363 28(19)	0.597 99(59)	C(25C)	0.065 71(33)	0.292 81(12)	0.411 44(30)
C(5C)	0.455 32(31)	0.337 17(12)	0.518 33(36)	C(26C)	−0.045 23(33)	0.294 06(12)	0.405 89(30)
C(6C)	0.414 95(31)	0.307 24(12)	0.445 46(36)	C(27C)	−0.09 609(33)	0.31 059(12)	0.307 54(30)
C(7C)	0.298 25(53)	0.298 87(27)	0.436 71(68)	C(28C)	−0.036 01(33)	0.32 587(12)	0.214 74(30)
C(8C)	0.247 63(49)	0.309 40(24)	0.325 27(59)	C(29C)	0.026 43(32)	0.424 13(12)	0.041 28(26)
C(9C)	0.125 78(33)	0.308 07(12)	0.318 64(30)	C(30C)	−0.059 79(32)	0.450 25(12)	0.040 17(26)
C(10C)	0.074 92(33)	0.324 60(12)	0.220 29(30)	C(31C)	−0.097 85(32)	0.465 85(12)	0.146 03(26)
C(11C)	0.137 55(48)	0.342 12(18)	0.121 07(55)	C(32C)	−0.049 68(32)	0.455 33(12)	0.253 01(26)

ionization experiments were carried out, clusters of compounds of Table 1 and ammonia were observed (*e.g.*, compound **18** in positive-Cl NH_3, present peaks at 748 and 763 Th).*

Reaction Between α,α′-Dibromo-o-xylene and Sodium.—To a solution of α,α′-dibromo-*o*-xylene (12.0 g, 45 mmol) in dry dioxane (450 cm^3) was added sodium (8.3 g, 361 mmol), finely dispersed in dry dioxane. The resultant suspension was heated at reflux temperature acquiring a deep blue colour. After 52 h the solvent was evaporated off under reduced pressure. The solid obtained was taken up in benzene (4.150 cm^3), treated with ethanol to destroy the excess of sodium, and the mixture neutralized with 50% aqueous hydrochloric acid. The organic layer was then separated and the solvent eliminated. The residue was treated again with dichloromethane and dried over anhydrous Na_2SO_4 affording 5.6 g of crude product after evaporation of the organic solvent. Column chromatography on silica gel (Merck 60, 70–230 mesh) with hexane and mixtures of hexane–benzene of increasing polarity gave the products shown in Table 1.

When the reaction was performed under similar conditions by refluxing for 24 h in toluene (450 cm^3) instead of dioxane, a residue of 10.4 g was isolated by extraction with diethyl ether, from which only acyclic hydrocarbons were identified: xylene (60%), 1,2-di(*o*-tolyl)ethane (**13**),[17] $R_f(CHCl_3)$ 0.71; $\delta(CDCl_3)$: 7.3–7.1 (8 H, m, ArH), 2.89 (4 H, s, $ArCH_2CH_2Ar$) and 2.35 (6 H, s, ArMe); 1,2-bis(*o*-ethoxymethylphenyl)ethane (**17**), oil, $M^{\cdot+}$ 298 ($C_{20}H_{26}O_2$) (Calc.: C, 80.50; H, 8.8. Found: C, 80.33; H, 8.91) $R_f(CHCl_3)$: 0.65; $\delta(CDCl_3)$: 7.2–7.1 (8 H, m, ArH), 4.50 (4 H, s, $ArCH_2O$), 3.56 (4 H, q, OCH_2Me), 2.34 (4 H, s, $ArCH_2CH_2Ar$) and 1.25 (6 H, t, OCH_2Me); and α,α′-diethoxy-*o*-xylene (**18**), oil, $M^{\cdot+}$ 194 ($C_{12}H_{18}O_2$) (Calc.: C, 74.2; H, 9.3. Found: C, 73.97; H, 9.52) $R_f(CHCl_3)$: 0.46; $\delta(CDCl_3)$: 7.2–7.4 (8 H, m, ArH), 4.58 (4 H, s, $ArCH_2O$), 3.54 (4 H, q, OCH_2Me) and 1.24 (6 H, t, OCH_2Me).

6,7,13,14-*Tetrahydrodipyrido*[1,2-a:1,2-e]*diazocinium Dibromide* (**11**).—This was prepared according to the literature[21] by dimerization of 2-(β-bromoethyl)pyridine in 77% yield, m.p. 239–240 °C (from methanol–water, 2:1); lit.[21]: 238–240 °C; R_f(ethyl ether): 0.52. This compound presents a mass spectrum with the most intense peak at 211 Th (C^{++}–H^+) both using chemical ionization[30] and thermospray positive mode.

Crystallography.—Cell parameters and orientation matrices were obtained by least-squares refinement using 30 reflections in the range $20 < \theta < 35°$. The data collection, at room temperature, was performed for the four compounds on a Siemens AED diffractometer using $\theta/2\theta$ scan mode, scan speed 3–12° min^{-1}, scan width (1.20 + 0.14 tan θ) and θ in the range 3–70°. One standard reflection was measured every 100. The reflections were corrected for Lorentz and polarization; absorption correction was applied for compound $C_{14}H_{16}N_2Br_2 \cdot 2H_2O$ and $C_{32}H_{32}$ following Uguzzoli.[31] All the calculations were performed on the Gould computer system of the *Centro di Strutturistica Diffrattometrica del CNR, Parma,* Italy. The structures were solved using the SHELXS program;[32] the refinement (anisotropic for heavy atoms and rigid-body constraint for the phenyl ring, isotropic for the hydrogens) was performed by full-matrix least-squares (block-matrix for the $C_{32}H_{32}$ compound owing to the high number of parameters to be refined) using the program SHELX76 with the form factors included.[33] Geometric calculations were performed with PARST[34] and CRYSRULER package;[35] drawings were made with the PLUTO[24] program through CRYSRULER package.†[35] Atomic coordinates and selected bond distances and bond angles are given in Tables 9 and 10.

NMR Spectroscopy.—The NMR spectra were recorded on a Bruker AC200, working at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C, and a Varian unity, operating at 499.84 MHz for ^1H, spectrometers. Both pieces of apparatus were equipped with variable-temperature units. The temperature of the probe was calibrated by the methanol standard method (±0.5 K). ^1H and ^{13}C chemical shifts (δ) are given from internal TMS with an accuracy of ±0.01 and ±0.1 ppm, respectively. Coupling constants *J* were measured with a digital resolution of 0.2 and 0.6 Hz, respectively. The data acquisition parameters for the heteronuclear (^1H–^{13}C) 2D-correlations experiments were F_1

* 1 Th (thomson) = a mass/charge ratio of 1 Da per unit of atomic charge. *Rapid. Commun. Mass. Spectrum.*, 1991, **5**, 93.

† Lists of thermal components, hydrogen parameters and full lists of bond distances, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

Table 10 Selected bond distances/Å and bond angles/° for compounds **1**, **11**, **12** and **16**

1

C(1)–C(2)	1.395(2)	C(3)–C(4)	1.395(2)	C(6)–C(1)–C(7)	118.2(1)	C(2)–C(3)–C(4)	120.0(1)
C(1)–C(6)	1.395(2)	C(4)–C(5)	1.395(2)	C(2)–C(1)–C(7)	121.8(1)	C(3)–C(4)–C(5)	120.0(1)
C(1)–C(7)	1.514(2)	C(5)–C(6)	1.395(2)	C(2)–C(1)–C(6)	120.0(1)	C(4)–C(5)–C(6)	120.0(1)
C(2)–C(3)	1.395(2)	C(7)–C(8A)	1.553(2)	C(1)–C(2)–C(8)	121.2(1)	C(1)–C(7)–C(8A)	114.7(1)
C(2)–C(8)	1.518(2)			C(1)–C(2)–C(3)	120.0(1)	C(2)–C(8)–C(7A)	114.8(1)
				C(3)–C(2)–C(8)	118.7(1)		

11

N(1)–C(2)	1.372(5)	C(4)–C(5)	1.374(7)	C(2)–N(1)–C(6)	120.2(3)	C(5)–C(4)–H(4)	118.6(5)
N(1)–C(6)	1.361(6)	C(5)–C(6)	1.377(6)	N(1)–C(2)–C(8)	119.6(3)	C(4)–C(5)–C(6)	119.1(4)
N(1)–C(7)	1.483(6)	C(7)–C(8A)	1.542(5)	N(1)–C(2)–C(3)	119.2(3)	N(1)–C(6)–C(5)	121.1(4)
C(2)–C(3)	1.368(6)			C(3)–C(2)–C(8)	121.1(3)	N(1)–C(7)–C(8A)	112.7(3)
C(2)–C(8)	1.496(5)	C(6)–N(1)–C(7)	119.1(3)	C(2)–C(3)–C(4)	120.9(4)	C(2)–C(8)–C(7A)	114.5(3)
C(3)–C(4)	1.383(7)	C(2)–N(1)–C(7)	120.7(3)	C(3)–C(4)–C(5)	119.5(4)		

12

C(1)–C(2)	1.395(2)	C(8)–C(9)	1.522(3)	C(3)–C(2)–C(16)	117.4(2)	C(7)–C(8)–C(9)	112.3(2)
C(1)–C(12)	1.521(2)	C(9)–C(10)	1.395(2)	C(2)–C(3)–C(4)	117.5(2)	C(8)–C(9)–C(21)	116.8(2)
C(2)–C(3)	1.517(3)	C(10)–C(11)	1.518(3)	C(3)–C(4)–C(5)	110.6(2)	C(8)–C(9)–C(10)	123.1(2)
C(3)–C(4)	1.538(4)	C(11)–C(12)	1.533(4)	C(4)–C(5)–C(17)	117.4(2)	C(9)–C(10)–C(11)	123.0(2)
C(4)–C(5)	1.523(3)			C(4)–C(5)–C(6)	122.5(2)	C(11)–C(10)–C(24)	117.0(2)
C(5)–C(6)	1.395(2)	C(12)–C(1)–C(13)	117.7(2)	C(5)–C(6)–C(7)	123.6(2)	C(10)–C(11)–C(12)	111.8(2)
C(6)–C(7)	1.520(3)	C(2)–C(1)–C(12)	122.3(2)	C(7)–C(6)–C(20)	116.3(2)	C(1)–C(12)–C(11)	114.6(2)
C(7)–C(8)	1.537(4)	C(1)–C(2)–C(3)	122.6(2)	C(6)–C(7)–C(8)	113.7(2)		

16

C(1)–C(2)	1.395(5)	C(1A)–C(2A)	1.395(4)	C(1B)–C(2B)	1.395(5)	C(1C)–C(2C)	1.395(5)
C(1)–C(16)	1.532(6)	C(1A)–C(16A)	1.518(6)	C(1B)–C(16B)	1.523(6)	C(1C)–C(16C)	1.536(6)
C(2)–C(3)	1.492(6)	C(2A)–C(3A)	1.558(7)	C(2B)–C(3B)	1.529(7)	C(2C)–C(3C)	1.537(7)
C(3)–C(4)	1.585(7)	C(3A)–C(4A)	1.491(9)	C(3B)–C(4B)	1.533(9)	C(3C)–C(4C)	1.519(9)
C(4)–C(5)	1.533(7)	C(4A)–C(5A)	1.509(8)	C(4B)–C(5B)	1.518(8)	C(4C)–C(5C)	1.542(6)
C(5)–C(6)	1.395(5)	C(5A)–C(6A)	1.395(5)	C(5B)–C(6B)	1.395(5)	C(5C)–C(6C)	1.395(6)
C(6)–C(7)	1.516(7)	C(6A)–C(7A)	1.541(7)	C(6B)–C(7B)	1.500(7)	C(6C)–C(7C)	1.495(8)
C(7)–C(8)	1.534(9)	C(7A)–C(8A)	1.492(10)	C(7B)–C(8B)	1.468(10)	C(7C)–C(8C)	1.452(11)
C(8)–C(9)	1.542(7)	C(8A)–C(9A)	1.523(7)	C(8B)–C(9B)	1.548(7)	C(8C)–C(9C)	1.532(7)
C(9)–C(10)	1.395(6)	C(9A)–C(10A)	1.395(6)	C(9B)–C(10B)	1.395(5)	C(9C)–C(10C)	1.395(5)
C(10)–C(11)	1.515(7)	C(10A)–C(11A)	1.495(7)	C(10B)–C(11B)	1.523(7)	C(10C)–C(11C)	1.496(7)
C(11)–C(12)	1.523(9)	C(11A)–C(12A)	1.566(9)	C(11B)–C(12B)	1.552(9)	C(11C)–C(12C)	1.543(9)
C(12)–C(13)	1.506(7)	C(12A)–C(13A)	1.528(7)	C(12B)–C(13B)	1.535(7)	C(12C)–C(13C)	1.515(7)
C(13)–C(14)	1.395(4)	C(13A)–C(14A)	1.395(4)	C(13B)–C(14B)	1.395(4)	C(13C)–C(14C)	1.395(5)
C(14)–C(15)	1.512(6)	C(14A)–3(15A)	1.534(6)	C(14B)–C(15B)	1.533(6)	C(14C)–C(15C)	1.533(6)
C(15)–C(16)	1.544(8)	C(15A)–C(16A)	1.558(8)	C(15B)–C(16B)	1.521(8)	C(15C)–C(16C)	1.542(8)

C(16)–C(1)–C(17)	115.7(3)	C(5A)–C(6A)–C(7A)	121.3(4)	C(10B)–C(11B)–C(12B)	113.2(4)
C(2)–C(1)–C(16)	124.3(3)	C(7A)–C(6A)–C(24A)	118.6(4)	C(11B)–C(12B)–C(13B)	111.7(5)
C(1)–C(2)–C(3)	119.6(4)	C(6A)–C(7A)–C(8A)	111.0(5)	C(12B)–C(13B)–C(29B)	117.3(4)
C(3)–C(2)–C(20)	120.4(3)	C(7A)–C(8A)–C(9A)	117.6(5)	C(12B)–C(13B)–C(14B)	122.6(4)
C(2)–C(3)–C(4)	112.4(3)	C(8A)–C(9A)–C(25A)	119.5(4)	C(13B)–C(14B)–C(15B)	123.5(4)
C(3)–C(4)–C(5)	115.2(4)	C(8A)–C(9A)–C(10A)	120.5(4)	C(15B)–C(14B)–C(32B)	116.4(3)
C(4)–C(5)–C(21)	117.6(4)	C(9A)–C(10A)–C(11A)	120.2(4)	C(14B)–C(15B)–C(16B)	112.7(4)
C(4)–C(5)–C(6)	122.2(4)	C(11A)–C(10A)–C(28A)	119.7(4)	C(1B)–C(16B)–C(15B)	112.4(4)
C(5)–C(6)–C(7)	123.0(4)	C(10A)–C(11A)–C(12A)	115.1(5)	C(16C)–C(1C)–C(17C)	115.3(3)
C(7)–C(6)–C(24)	117.0(4)	C(11A)–C(12A)–C(13A)	112.3(5)	C(2C)–C(1C)–C(16C)	124.7(3)
C(6)–C(7)–C(8)	108.9(5)	C(12A)–C(13A)–C(29A)	117.0(4)	C(1C)–C(2C)–C(3C)	120.9(4)
C(7)–C(8)–C(9)	116.2(5)	C(12A)–C(13A)–C(14A)	123.0(4)	C(3C)–C(2C)–C(20C)	119.1(3)
C(8)–C(9)–C(25)	121.9(4)	C(13A)–C(14A)–C(15A)	123.4(4)	C(2C)–C(3C)–C(4C)	112.3(5)
C(8)–C(9)–C(10)	118.1(4)	C(15A)–C(14A)–C(32A)	116.6(3)	C(3C)–C(4C)–C(5C)	112.3(5)
C(9)–C(10)–C(11)	123.6(4)	C(14A)–C(15A)–C(16A)	112.9(4)	C(4C)–C(5C)–C(21C)	116.6(4)
C(11)–C(10)–C(28)	116.4(4)	C(1A)–C(16A)–C(15A)	111.4(4)	C(4C)–C(5C)–C(6C)	123.3(4)
C(10)–C(11)–C(12)	113.3(5)	C(16B)–C(1B)–C(17B)	115.6(3)	C(5C)–C(6C)–C(7C)	121.8(4)
C(11)–C(12)–C(13)	113.5(5)	C(2B)–C(1B)–C(16B)	124.4(3)	C(7C)–C(6C)–C(24C)	118.1(5)
C(12)–C(13)–C(29)	116.3(4)	C(1B)–C(2B)–C(3B)	120.8(4)	C(6C)–C(7C)–C(8C)	115.8(5)
C(12)–C(13)–C(14)	123.7(4)	C(3B)–C(2B)–C(20B)	119.2(3)	C(7C)–C(8C)–C(9C)	117.8(5)
C(13)–C(14)–C(15)	123.2(4)	C(2B)–C(3B)–C(4B)	113.2(5)	C(8C)–C(9C)–C(25C)	121.3(4)
C(15)–C(14)–C(32)	116.7(3)	C(3B)–C(4B)–C(5B)	114.0(5)	C(8C)–C(9C)–C(10C)	118.6(4)
C(14)–C(15)–C(16)	112.3(4)	C(4B)–C(5B)–C(21B)	116.3(4)	C(9C)–C(10C)–C(11C)	121.0(4)
C(1)–C(16)–C(15)	112.1(4)	C(4B)–C(5B)–C(6B)	123.6(4)	C(11C)–C(10C)–C(28C)	119.0(4)
C(16A)–C(1A)–C(17A)	115.5(3)	C(5B)–C(6B)–C(7B)	121.7(4)	C(10C)–C(11C)–C(12C)	113.7(5)
C(2A)–C(1A)–C(16A)	124.4(3)	C(7B)–C(6B)–C(24B)	118.2(4)	C(11C)–C(12C)–C(13C)	113.2(5)
C(1A)–C(2A)–C(3A)	122.0(4)	C(6B)–C(7B)–C(8B)	112.9(5)	C(12C)–C(13C)–C(29C)	116.5(4)
C(3A)–C(2A)–C(20A)	118.0(3)	C(7B)–C(8B)–C(9B)	117.7(5)	C(12C)–C(13C)–C(14C)	123.4(4)
C(2A)–C(3A)–C(4A)	113.9(4)	C(8B)–C(9B)–C(25B)	120.2(4)	C(13C)–C(14C)–C(15C)	123.4(4)
C(3A)–C(4A)–C(5A)	114.8(5)	C(8B)–C(9B)–C(10B)	119.7(4)	C(15C)–C(14C)–C(32C)	116.6(3)
C(4A)–C(5A)–C(21A)	115.1(4)	C(9B)–C(10B)–C(11B)	121.6(4)	C(14C)–C(15C)–C(16C)	112.7(4)
C(4A)–C(5A)–C(6A)	124.8(4)	C(11B)–C(10B)–C(28B)	118.4(4)	C(1C)–C(16C)–C(15C)	111.9(4)

domain (SI1: 512W, SW1: 900 Hz, relaxation delay D1: 1), F_2 domain (SI2: 4 K, SW2: 7143 Hz) number of transients per FID, NS: 32, number of preparatory dummy transients per FID, DS: 0.

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References

1 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.
2 W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 1945, 27.
3 D. W. Jones and W. S. McDonald, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2257.
4 R. M. Wilson, K. Hanneman, K. Peters and E. M. Peters, *J. Am. Chem. Soc.*, 1987, **100**, 4741.
5 P. G. Jones, G. Bodwell and H. Hopf, *Z. Naturforsch., Teil B*, 1990, **45**, 1213.
6 R. L. Barnett and R. E. Davis, *Acta Crystallogr., Sect. B*, 1970, **26**, 1026.
7 H. Irngartinger and W. R. K. Reibel, *Acta Crystallogr., Sect. B*, 1981, **37**, 1724.
8 P. Destro, T. Pilati and M. Simonetta, *Acta Crystallogr., Sect. B*, 1977, **33**, 447.
9 J. A. Moore and F. A. L. Anet, in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 7, ch. 5.19, p. 653.
10 R. P. Arshinova, *Russ. Chem. Rev.*, 1988, **57**, 1142.
11 W. D. Ollis, J. F. Stoddart and I. O. Sutherland, *Tetrahedron*, 1974, **30**, 1903.
12 D. J. Brickwood, W. D. Ollis, J. Stephanidou Stephanatou and J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1398 and references therein.
13 M. C. Aversa, P. Bonaccorsi, P. Giannetto and D. A. Leigh, *Tetrahedron*, 1989, **45**, 6857.
14 P. Sohár, I. Kövesdi, J. Szabó, A. Katócs, L. Fodor, E. Szücs, G. Bernáth and J. Tamás, *Magn. Reson. Chem.*, 1989, **27**, 760.
15 J. Elguero, A. R. Katritzky, B. S. El-Osta, R. L. Harlow and S. H. Simonsen, *J. Chem. Soc., Perkin Trans. 1*, 1976, 312.
16 C. Foces-Foces, F. H. Cano, P. Cabildo, R. M. Claramunt and J. Elguero, *Acta Crystallogr., Sect. C*, 1991, **47**, 2583.
17 A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, 1951, **73**, 1668.
18 J. B. Hendrickson, *J. Am. Chem. Soc.*, 1967, **89**, 7047.
19 P. Crossley, A. P. Downing, M. Nógrády, A. Braga de Oliveira, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1973, 205.
20 F. Sauriol-Lord and M. St-Jacques, *Can. J. Chem.*, 1975, **53**, 3768.
21 V. Boekelheide and W. Feely, *J. Am. Chem. Soc.*, 1958, **80**, 2217.
22 E. Müller and G. Röscheisen, *Chem. Ber.*, 1957, **90**, 543.
23 R. B. Bates and C. A. Ogle, *J. Org. Chem.*, 1982, **47**, 3949.
24 W. D. S. Motherwell and W. Clegg, PLUTO: Program for plotting molecular and crystal structures, University of Cambridge, England, 1978.
25 A. Gavezzotti, OPEC: Organic Packing Energy Calculations and Volume Analysis, Version 1990, University of Milan (see also *J. Am. Chem. Soc.*, 1983, **105**, 5220).
26 H. O. Kalinowski, S. Berger and S. Braun, *Carbon-13 NMR Spectroscopy*, Wiley: New York, 1988.
27 M. L. Jimeno, J. Elguero, R. M. Claramunt, J. L. Lavandera, P. Domiano and P. Cozzini, unpublished results.
28 N. L. Allinger and J. T. Sprague, *Tetrahedron*, 1975, **31**, 21.
29 M. J. C. Crabbé and J. R. Appleyard, Desktop Molecular Modeler, Version 1.2, Oxford University Press, 1990.
30 J. L. Aubagnac, R. M. Claramunt, J. L. Lavandera and J. Elguero, *Bull. Soc. Chim. Belg.*, 1991, **100**, 459.
31 F. Ugozzoli, *Comput. Chem.*, 1987, 11, 109.
32 G. M. Sheldrick, SHELXS: Program for crystal structure solution, University of Göttingen, Germany, 1980.
33 G. M. Sheldrick, SHELX76: Program for crystal structure determination, University of Cambridge, England, 1976.
34 M. Nardelli, PARST, *Comput. Chem.*, 1983, **7**, 95.
35 C. Rizzoli, V. Sangermano, G. Calestani and G. D. Andreetti, CRYSRULER: An integrated system of computer programs for crystal structure analysis on a personal computer, *J. Appl. Cryst.*, 1987, **20**, 436.

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