

Structure of 1,5-Bis(dimethylamino)-1,5-diphenylpentadienylium Perchlorate and Modelling of Pentadienylium Salts (Cyanine Dyes)

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(Received 23 December 1994; accepted 8 September 1995)

Abstract

$C_{21}H_{25}N_2^+.ClO_4^-$ (orange crystals), $M_r = 404.9$, orthorhombic; $P2_12_12_1$, $a = 7.810(2)$, $b = 15.007(3)$, $c = 18.326(3)$ Å, $V = 2147.8(7)$ Å³. Graphite-monochromated Mo $K\alpha$ source at room temperature; $\lambda = 0.71069$ Å, $\mu = 0.22$ mm⁻¹, $Z = 4$; $F(000) = 856$, $D_x = 1.25$ g cm⁻³, $R = 0.057$ for 1392 independent data. As for the unsubstituted pentamethinium dyes, the chain lies in an all-*trans* planar configuration. Molecular modelling calculations reproduce the X-ray structure with good accuracy, even in the case of more crowded pentadienylium cations, *i.e.* 1,5-bis(dimethylamino)-1,3,5-triphenylpentadienylium perchlorate.

1. Introduction

Organic conjugated pentamethinium (pentadienylium) salts present original chemical and physical properties due to their particular electronic and spatial structures. The use of their optical properties in fluorescence for biological purposes (Rink & Hladky, 1982) as sensitizing agents in plate emulsions (Hamer, 1964) or more recently in optical memories (Emmelius, Pawlovski & Vollmann, 1989) is to be emphasized. The progress of the colour photography is now assessed by a continuum of patents (several hundred per year) devoted to the enlargement of spectral sensitization and to improve the sharpness and reduce the grain. In the optical memories field, several hundred papers and patents appeared mainly over the last 2 years (*Chem. Abstr.* source). This denotes the rising industrial competition for progress in optical data storage densities and read–write efficiency, not only for professional use but also for consumer electronic devices.

Thus, the knowledge of the structure of new compounds in these series, mainly in the solid state, and their spatial organization may lead to new applications.

Another interesting feature is to preview by modelling the structure of a projected compound and thus to design more efficiently the synthesis of desired properties.

The aim of the work presented here is first to describe a new crystallographic structure obtained in these series

for 1,5-bis(dimethylamino)-1,5-diphenylpentadienylium perchlorate (2). In a second stage this structure, together with (1) and (2) previously obtained, will be modelled using the *InsightII* program (Biosym Technologies, 1994) in order to compare the experimental and calculated results.

2. Experimental

Orange crystals of (2) were obtained as previously described, from the corresponding pyrylium salt and tris(dimethylamino)arsane (Madaule, Ramarohetra, Wolf, Declercq & Dubourg, 1991). Suitable crystals were obtained by slow recrystallization from ethanol.

Other synthetic methods leading to the same compound were recently developed in our group (Madaule, Ramarohetra & Wolf, 1992; Payrastré, Obaya, Madaule & Wolf, 1994). See Table 1 for full experimental details. The structure was determined by direct methods (*MULTAN80*; Main *et al.*, 1980). The most probable set of phases revealed, in the corresponding Fourier synthesis, almost all the atoms of the molecule. Full-matrix least-squares (*SHELX76*; Sheldrick, 1976) was used for the final refinement on *F*. C, N, Cl and O atoms are anisotropic. The H atoms bonded to the chain C2, C3 and C4 atoms are revealed by a difference-Fourier map and isotropically refined. The remaining H atoms are in theoretical positions.

The fractional coordinates, distances and valence angles are given in Tables 2 and 3, respectively.*

3. Results and discussion

3.1. Crystal structure of (2): cf. Fig. 1

As for the corresponding unsubstituted pentadienylium salt (1), the chain N1...N2 is in a planar all-*E* polyenic configuration. Several X-ray structure determinations of the allotropic yellow (Seltzer &

* Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: HU0429). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

Crystal data	
Chemical formula	C ₂₁ H ₂₅ N ₂ ⁺ ClO ₄ ⁻
Chemical formula weight	404.9
Cell setting	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	7.810 (2)
<i>b</i> (Å)	15.007 (3)
<i>c</i> (Å)	18.326 (3)
<i>V</i> (Å ³)	2147.8 (7)
<i>Z</i>	4
<i>D_s</i> (Mg m ⁻³)	1.25
Radiation type	Mo <i>K</i> α
Wavelength (Å)	0.71073
No. of reflections for cell parameters	19
θ range (°)	10–27
μ (mm ⁻¹)	0.22
Temperature (K)	297
Crystal form	Prism
Crystal size (mm)	0.40 × 0.30 × 0.25
Crystal color	Orange
Data collection	
Diffractometer	Huber
Data collection method	ω -2 θ
Absorption correction	None
No. of measured reflections	2424
No. of independent reflections	2424
No. of observed reflections	1392
Criterion for observed reflections	$I > 2.5\sigma(I)$
θ_{\max} (°)	26
Range of <i>h, k, l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 17 0 → <i>l</i> → 22
No. of standard reflections	1
Frequency of standard reflections	Every 50 reflections
Intensity decay (%)	Not significant
Refinement	
Refinement on	<i>F</i>
<i>R</i>	0.057
<i>wR</i>	0.059
<i>S</i>	1.66
No. of reflections used in refinement	1392
No. of parameters used	267
H-atom treatment	See text
Weighting scheme	$w = 1/[\sigma^2(F) + 0.00074F^2]$
$(\Delta/\sigma)_{\max}$	0.2
$\Delta\rho_{\max}$ (e Å ⁻³)	0.27
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.22
Extinction method	None
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

Matthews, 1976; Chentli-Benchikha, Declercq, Germain & Van Meerssche, 1977) or orange forms (Sieber, Kutschabsky & Kulpe, 1974; Honda, Katayama & Tanaka, 1986) of (2) are published, which differ only in the packing of the cation chains in the lattice and in the position of the anion. In all cases the chain has a planar all-*trans* configuration. This configuration is also observed for other anions, such as Cl⁻, rather than for ClO₄⁻ (Ziemer & Kulpe, 1975).

The maximum distance of one atom of the chain to the mean plane is 0.08 Å, whereas the C1—C5 length is 4.89 Å, compared with the sum of the interatomic distances, 5.5 Å, or better to the sum of their projection on the C1...C5 axis, 4.78 Å. The torsion angles

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

	$B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$			B_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
Cl	0.3533 (3)	0.4433 (1)	0.9542 (1)	5.3 (1)
O1	0.3889 (14)	0.4027 (7)	0.8888 (5)	14.1 (3)
O2	0.2205 (10)	0.5072 (5)	0.9401 (4)	9.5 (2)
O3	0.4887 (11)	0.4958 (6)	0.9786 (4)	11.4 (2)
O4	0.2970 (10)	0.3836 (5)	1.0091 (5)	10.4 (2)
N1	0.8212 (8)	0.7373 (4)	0.8962 (3)	5.3 (1)
N2	0.2593 (8)	1.1182 (4)	0.9117 (3)	4.4 (1)
C1	0.6790 (9)	0.7797 (4)	0.8773 (3)	3.9 (1)
C2	0.6340 (10)	0.8625 (4)	0.9054 (4)	3.9 (1)
C3	0.4870 (9)	0.9071 (4)	0.8863 (4)	3.4 (1)
C4	0.4457 (10)	0.9900 (5)	0.9098 (4)	4.1 (1)
C5	0.3028 (9)	1.0401 (4)	0.8836 (3)	3.5 (1)
C6	0.5646 (9)	0.7360 (4)	0.8225 (3)	3.6 (1)
C7	0.5540 (10)	0.7692 (5)	0.7511 (4)	4.4 (1)
C8	0.4431 (11)	0.7305 (5)	0.7022 (4)	5.1 (1)
C9	0.3426 (10)	0.6598 (5)	0.7223 (4)	5.1 (1)
C10	0.3496 (10)	0.6272 (5)	0.7921 (4)	4.7 (1)
C11	0.4626 (10)	0.6654 (5)	0.8420 (4)	4.4 (1)
C12	0.2049 (9)	1.0044 (4)	0.8208 (4)	3.5 (1)
C13	0.0307 (9)	0.9861 (5)	0.8288 (4)	4.5 (1)
C14	-0.0578 (11)	0.9480 (5)	0.7726 (5)	5.7 (2)
C15	0.0206 (12)	0.9262 (5)	0.7082 (5)	5.5 (2)
C16	0.1943 (11)	0.9444 (5)	0.6996 (4)	5.1 (1)
C17	0.2827 (10)	0.9824 (5)	0.7560 (4)	4.1 (1)
C18	0.9375 (13)	0.7758 (6)	0.9513 (5)	8.1 (2)
C19	0.8779 (13)	0.6532 (6)	0.8641 (6)	8.5 (3)
C20	0.1353 (11)	1.1790 (5)	0.8801 (5)	5.6 (2)
C21	0.3369 (13)	1.1500 (6)	0.9807 (5)	7.1 (2)
H2	0.7038 (77)	0.8901 (40)	0.9416 (32)	4 (1)
H3	0.4110 (72)	0.8749 (37)	0.8592 (29)	3 (1)
H4	0.5220 (83)	1.0109 (38)	0.9394 (32)	3 (1)

Table 3. *Selected geometric parameters (Å, °)*

Cl—O1	1.372 (7)	C7—C6	1.403 (9)
Cl—O2	1.435 (7)	C11—C6	1.373 (9)
Cl—O3	1.392 (7)	C8—C7	1.375 (9)
Cl—O4	1.418 (7)	C9—C8	1.371 (11)
C1—N1	1.326 (9)	C10—C9	1.371 (10)
C18—N1	1.477 (10)	C11—C10	1.394 (10)
C19—N1	1.461 (10)	C13—C12	1.396 (10)
C5—N2	1.324 (8)	C17—C12	1.375 (9)
C20—N2	1.451 (9)	C14—C13	1.366 (10)
C21—N2	1.480 (9)	C15—C14	1.369 (11)
C2—C1	1.391 (9)	C16—C15	1.393 (12)
C6—C1	1.496 (9)	C17—C16	1.367 (10)
C3—C2	1.374 (9)	H2—C2	0.95 (6)
C4—C3	1.356 (9)	H3—C3	0.91 (6)
C5—C4	1.429 (10)	H4—C4	0.86 (6)
C12—C5	1.481 (9)		
O2—Cl—O1	106.6 (6)	C11—C6—C1	120.6 (6)
O3—Cl—O1	112.2 (6)	C11—C6—C7	118.9 (6)
O3—Cl—O2	103.2 (5)	C8—C7—C6	119.7 (7)
O4—Cl—O1	113.7 (6)	C9—C8—C7	120.8 (7)
O4—Cl—O2	109.0 (4)	C10—C9—C8	120.4 (7)
O4—Cl—O3	111.4 (5)	C11—C10—C9	119.3 (7)
C18—N1—C1	120.4 (6)	C10—C11—C6	120.9 (7)
C19—N1—C1	124.2 (6)	C13—C12—C5	119.5 (6)
C19—N1—C18	115.3 (7)	C17—C12—C5	122.0 (6)
C20—N2—C5	124.9 (6)	C17—C12—C13	118.3 (7)
C21—N2—C5	120.8 (6)	C14—C13—C12	119.8 (7)
C21—N2—C20	114.3 (6)	C15—C14—C13	121.6 (7)
C2—C1—N1	122.9 (6)	C16—C15—C14	119.1 (7)
C6—C1—N1	117.8 (6)	C17—C16—C15	119.2 (8)
C6—C1—C2	119.3 (6)	C16—C17—C12	122.0 (7)
C3—C2—C1	123.5 (7)	H2—C2—C1	120 (4)
C4—C3—C2	124.4 (7)	C3—C2—H2	116 (4)
C5—C4—C3	124.2 (7)	H3—C3—C2	115 (4)
C4—C5—N2	122.3 (6)	C4—C3—H3	120 (4)
C12—C5—N2	119.4 (6)	H4—C4—C3	112 (4)
C12—C5—C4	118.2 (6)	C5—C4—H4	124 (4)
C7—C6—C1	120.4 (6)		

within the chain differ from zero by less than $7(2)^\circ$. All C—C bonds in the chain are partially double, *i.e.* $1.356 < \text{C—C} < 1.429$, C1—N1 $1.326(9)$ and C5—N2 $1.324(8)$ Å. Moreover, for the seventh atom of the chain, the sum of the valence angles is in the range $360 \pm 0.8^\circ$.

The axes of the two phenyl substituents (lines C1—C6—C9 and C5—C12—C15, respectively) are closely parallel, as shown by the following interatomic distances: C1—C5 $4.89(1)$, C6—C12 $4.91(1)$ and C9—C15 $4.73(1)$ Å, whereas the angle between the phenyl planes is 51° .

Finally, examination of the shortest interatomic distances between the anion and the cation indicates only weak hydrogen bonding, *i.e.* O2—H10 $2.73(1)$ and O2—C10 $3.41(1)$ Å for interaction with the phenyl H atoms.

The interaction between the O atoms of the anion and the H atoms of the N methyls is obviously weaker than the previously reported results for the unsubstituted chain [Honda, Katayama & Tanaka, 1986; O2—C19 $(-1 + x, y, z)$ $3.73(1)$, O—C reported 3.27 and O2—H19 $(-1 + x, y, z)$ $2.84(1)$ Å]. Consequently, in the following the modelling of these structures will be accurately represented by calculation on the cation only.

The projections of the packing cell along the axes *OA*, *OB* or *OC* show a long-range organization. The dye cations are linearly arranged in two directions (Fig. 2). The angle between the two orientations ($74 \pm 0.2^\circ$) was estimated as the angle of the C1—C5 vectors of a cyanine cation in each configuration. In one direction the vectors lie in a plane along parallel rows, with the short-

est distances calculated at 2.8, 6.24 and $9.02 (\pm 0.1)$ Å. The mean plane of the dye (containing all atoms other than the out-of-plane phenyl carbons) creates an angle of $45 (\pm 1.5)^\circ$ with the plane containing the C1—C5 vectors, thus in two consecutive planes the dye is in an alternate perpendicular position.

3.2. Molecular modelling

Modelling calculations were performed on a Silicon Graphics Personal Iris 4D30 using the program *InsightII* (Biosym Technologies, 1994).

Owing to the cationic nature of these organic structures it was necessary to first determine the partial charges on each atom in a delocalized system bearing a (+1) total charge. This was realized by the Ampac—Mopac module. The final refinement of the structure was then obtained after minimization with the conjugate gradient algorithm of *Discover3.1* with the consistent valence force field (CVFF). In the last stage, rotational constraints were imposed [360° rotation of the C1—C2—C3—*R* and *R*—C3—C4—C5 dihedral angles, with *R* = H(C3) or *R* = C(Ph—C3)]. Molecular dynamics on 100 ps at 1000 K allowed the selection of one or several minima for which the corresponding conformers were minimized to obtain the lowest energy structure. The final geometry was then compared with the solid-state X-ray structure by docking and calculating the r.m.s. deviation in the position of the chain C atoms. This method was applied to three compounds in this series: (1) 1,5-

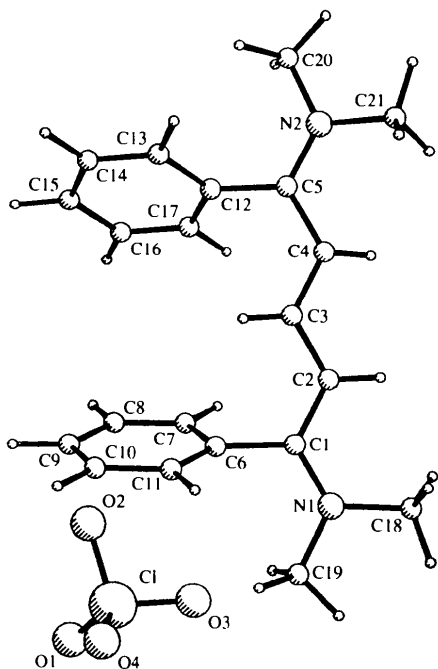


Fig. 1. Crystal structure of (2).

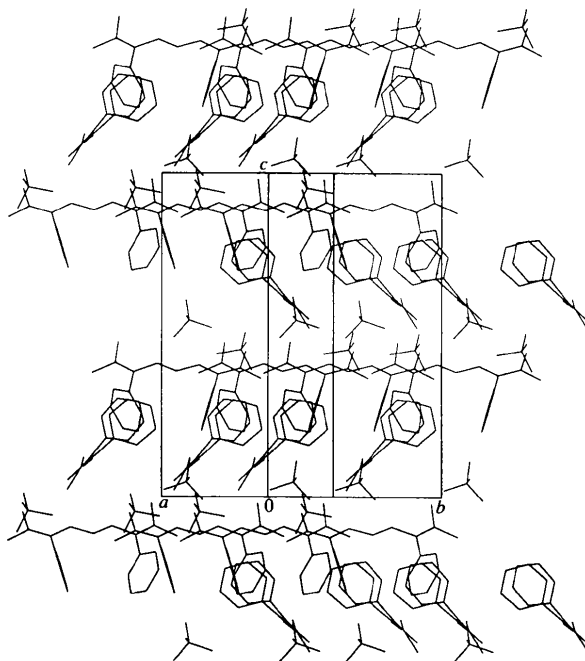
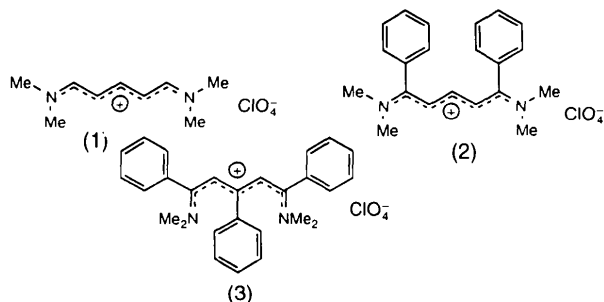


Fig. 2. Projection of the packing cell of (2), showing a linear arrangement.

Table 4. Calculated charges ($\times 1.6 \times 10^{-19} \text{C}$) and ^{13}C chemical shifts (Δ , p.p.m.)

	(1)	Δ	(2)	Δ	(3)	Δ
N1	-0.3292		-0.3485		-0.3700	
C1	0.2942	161.62	0.3462	170.10	0.3299	169.29
C2	-0.3034	102.77	-0.2984	106.36	-0.2925	109.39
C3	0.2333	162.52	0.2386	161.66	0.3121	169.03
C4	-0.3045	102.77	-0.3011	106.36	-0.2929	109.39
C5	0.2942	161.62	0.3526	170.10	0.3500	169.29
N2	-0.3321		-0.3363		-0.3590	

bis(dimethylamino)pentadienylium perchlorate, (2) 1,5-bis(dimethylamino)-1,5-diphenylpentadienylium perchlorate and (3) 1,5-bis(dimethylamino)-1,3,5-triphenylpentadienylium perchlorate.



3.3. Charge calculations

Table 4 shows the results of the Ampac-Mopac calculations of the partial charges on the pentadienylium chain C and N atoms.

The values obtained are in good agreement with those reported in the literature (Radechia *et al.*, 1972; Radechia, 1973; Radechia *et al.*, 1974), indicating a negative and positive charge alternation starting from the N atoms with C1, C3 and C5 positively charged.

These results are correlated with the experimental ^{13}C NMR chemical shifts. For the three compounds the change in charge between two consecutive C atoms

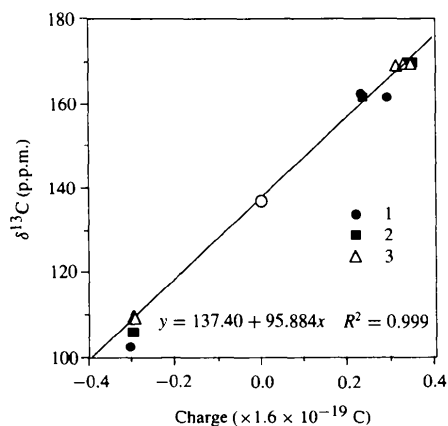


Fig. 3. Correlation charge ($\times 1.6 \times 10^{-19} \text{C}$)/ ^{13}C chemical shift (p.p.m.; CDCl_3) for (1), (2) and (3).

Table 5. Calculated energies (kJ) for (1), (2) and (3)

	(1)	(2)	(3)
Total	225.96	682.74	1288.99
Bond energy	10.80	98.85	153.07
θ	19.18	25.12	52.84
φ	0.42	68.45	159.14
Out-of-plane	0.004	0.03	2.93
Non-bond	52.34	318.03	417.88
Non-bond repulsion	147.08	624.29	896.31
Non-bond dispersion	-94.75	306.26	-478.43
Coulomb	143.23	172.24	503.13
R.m.s. derivative	0.001	0.00092	0.0011

(± 0.6) corresponds remarkably to the variation of the chemical shift (± 60 p.p.m.). In Fig. 3 are gathered the chemical shifts for all the chain C atoms of the three compounds and a good linear correlation is obtained. Moreover, the chemical shift value obtained for the null charge is that corresponding to the C2 atom of the butadiene (Gordon & Ford, 1972). It could be possible to individualize one type of C atom and to even obtain a satisfactory correlation (*i.e.* for C2 and C4), but in this case the number of points is too weak to fulfil statistical requirements.

3.4. Minimization

For the three compounds studied the minimization to a r.m.s. gradient of $< 0.004 \text{ kJ mol}^{-1}$ converged to

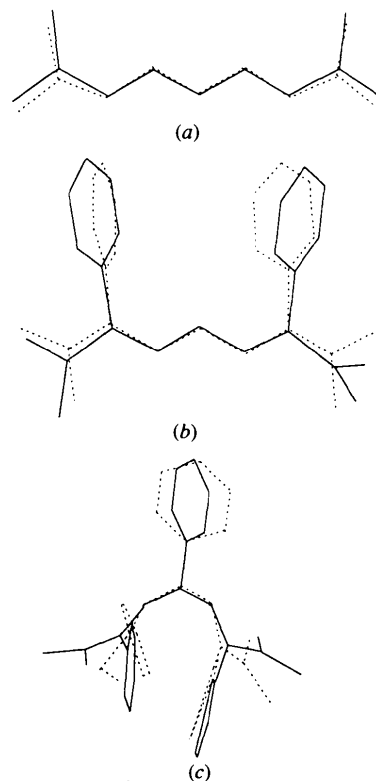


Fig. 4. Docking of the calculated (dotted lines) and X-ray structure of (a) (1), (b) (2) and (c) (3).

a unique conformation. The energy values obtained are summarized in Table 5.

Finally, the following schemes (Fig. 4) present the results obtained by docking in each case the calculated molecule (in dotted lines) and the available X-ray structure (in black; H atoms are omitted for clarity). For (1) and (2) we obtain an excellent fitting (r.m.s. = 0.0574 and 0.0715, respectively, on the position of the five chain C atoms), the major difference being observed for (2) in the angle between the phenyl planes. Even in the most crowded system (3), only the angular position of the C3 phenyl substituent presents a notable variation, whereas the helical carbon chain is accurately represented (r.m.s. = 0.152). Thus, it seems that in spite of the fact that the modelling represents a molecule in the gas phase, the results obtained can be suitably used in a prospective manner for a homogeneous series of compounds.

4. Conclusions

During this work we determined the solid-state X-ray structure of a new pentadienylum salt (2). Comparison with previously described compounds leads to the conclusion that the substitution by a phenyl on C1 and C5 has little influence on the preferred all-*E* configuration of the pentamethine chain. In striking contrast, the addition of a new substituent in position 3 enforces the chain in a non-planar all-*Z* configuration (*i.e.* for 3 the unit cell contains four molecules, two with a right helix chiral conformation and two with a left, forming a racemic mixture). Other authors (Reichardt, Engel, Allmann, Kucharczyk & Krestel, 1990) recently demonstrated that the presence of substituents in the C2 and C4 positions also introduce a distortion in the chain (*ZE* configuration).

Finally, careful molecular modelling may afford *a priori* structural information on the desired structures and will help us in defining new models in this series. The use of molecular mechanics in connection with X-ray structural determinations leads to an increasing number of publications with the aim of generalizing the structurally related properties through large series (Leuwerink, Harkema, Briels & Feil, 1993; Ciechanowicz-Rutkowska, Kiec-Konnowicz, Howard, Lieberman & Hursthouse, 1994).

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