

**STERICALLY CROWDED HETEROCYCLES. I. MOLECULAR STRUCTURE OF 3-CHAIN SUBSTITUTED 2-PHENYLIMIDAZO[1,2-*a*]PYRIDINIUM SALTS**

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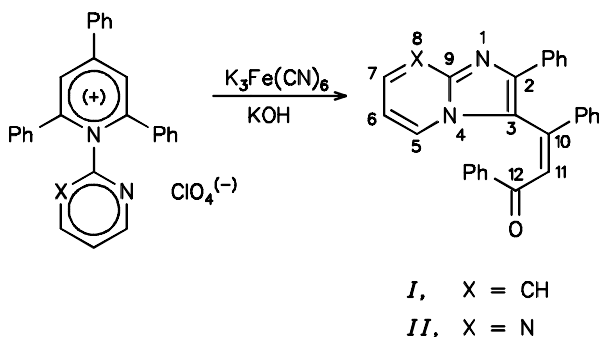
*Dedicated to Professor Milan Kratochvil on the occasion of his 70th birthday.*

2-Phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (*I*) was converted to corresponding 1-alkyl-2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridinium salts *III* – *VI* and 2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridinium perchlorate (*VII*). The protonation site is discussed in terms of calculated molecular energies of alternative cations. The X-ray structure analyses of enone *I* and its quaternary periodide *III* are reported and compared with the PM3 molecular optimizations. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra reveal well changes of molecular structures caused by the transformation of the base *I* into salts *III* – *VII*.

In connection with our interest in sterically crowded heterocyclic molecules the ferricyanide oxidation of 1-(2-heteroaryl)-2,4,6-triarylpyridinium salts<sup>1,2</sup> affording 2-phenyl-3-[(*Z*)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridine (*I*) or analogous imidazo [1,2-*a*]pyrimidine derivative *II* offers a general approach to this type of compounds (Scheme 1). In addition, a practical aspect of the research may be associated with a broad pharmacological activity of variously substituted imidazo[1,2-*a*]pyridines<sup>3–6</sup> and especially their quaternary salts being potent curariform agents<sup>7–9</sup>.

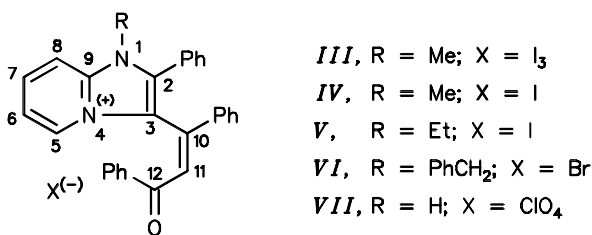
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The quaternization of unsaturated ketone *I* has been suggested to proceed at the N1 position<sup>2</sup> in agreement with the general behaviour of the imidazo[1,2-*a*]pyridine ring system<sup>10</sup>. The same regioselectivity was established for the protonation<sup>11</sup>.



SCHEME 1

In this paper the analogous transformations of enone *I* to salts *III* – *VII* are reported. In addition, crystal and molecular structures of compounds *I* and *III* have been investigated using the X-ray diffraction analysis and semiempirical quantum chemical calculations. The results are discussed in connection with complete assignments of high resolution <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the studied compounds. The hitherto performed MO studies on various imidazo[1,2-*a*]pyridines<sup>12</sup> are also enriched by the PM3 calculations of enone *I* and some related cations.



## EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block, the NMR spectra ( $\delta$ , ppm; *J*, Hz) were taken on a VARIAN VXR-400 instrument, (CD<sub>3</sub>)<sub>2</sub>SO was used as a solvent unless stated otherwise. The working frequency was 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. The preparation of compounds *I* and *II* was reported earlier<sup>1,2</sup>.

1-Methyl-2-phenyl-3-[(Z)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridinium Periodide (*III*)

A solution of iodine (0.1 g, 0.4 mmol) in methanol (10 ml) was added to iodide *IV* (0.16 g, 0.3 mmol) in methanol (10 ml). The precipitated product was let to free crystallization from methanol affording 0.18 g (57%) red crystals of *III* (Table I).

1-Alkyl-2-phenyl-3-[(Z)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridinium Halides *IV* – *VI*

Enone *I* (1 g, 2.5 mmol) and corresponding alkyl halogenide (40 – 160 mmol) in nitromethane (5 ml) were refluxed in dark for 2 – 4 h. After evaporation in vacuo the residue was crystallized from appropriate solvent. Yields and physicochemical data of products *IV* – *VI* are given in Table I.

2-Phenyl-3-[(Z)-1,3-diphenyl-3-oxopropenyl]imidazo[1,2-*a*]pyridinium Perchlorate (*VII*)

A solution of enone *I* (0.2 g) in ethanol (10 ml) was treated with 70% perchloric acid (1 ml). The precipitated crude product was crystallized from ethanol giving 0.2 g (80%) yellow crystals of *VII*.

X-Ray Analyses of Compounds *I* and *III*

*Enone I*: Monoclinic space group  $P2_1/n$ ,  $a = 11.914(1)$ ,  $b = 13.024(3)$ ,  $c = 13.968(2)$  Å,  $\beta = 100.25(1)^\circ$ ,  $V = 2132.7(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.25$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.07$  mm<sup>-1</sup>,  $F(000) = 840$ . The structure was solved by direct methods and anisotropically refined by full-matrix least-squares. The hydrogen atoms were fixed in calculated positions.

TABLE I  
Physico-chemical characteristics of salts *III* – *VII*

Compound	M.p., °C	Formula	Calculated/Found				
			Yield, %	(M.w.)	% C	% H	% N
<i>III</i>	178 – 179	C <sub>29</sub> H <sub>23</sub> I <sub>3</sub> N <sub>2</sub> O					
57	MeOH	(796.3)	43.75	2.91	3.52	47.82	
<i>IV</i> <sup>a</sup>	188 – 189	C <sub>29</sub> H <sub>23</sub> IN <sub>2</sub> O	43.76	2.89	3.45	48.03	
59	MeOH	(542.4)	64.22	4.27	5.17	23.40	
<i>V</i> <sup>a</sup>	112 – 115	C <sub>30</sub> H <sub>25</sub> IN <sub>2</sub> O	64.45	4.30	4.90	23.40	
72	Et <sub>2</sub> O <sup>b</sup>	(556.4)	64.76	4.53	5.03	22.81	
<i>VI</i> <sup>c</sup>	119 – 121	C <sub>35</sub> H <sub>28</sub> BrN <sub>2</sub> O	64.55	4.72	4.96	22.90	
70	Et <sub>2</sub> O <sup>b</sup>	(572.5)	73.43	4.93	4.89	13.96	
<i>VII</i>	225 – 226	C <sub>28</sub> H <sub>21</sub> ClN <sub>2</sub> O <sub>5</sub>	73.03	4.84	4.46	14.08	
80	EtOH	(500.9)	67.14	4.23	5.59	7.08	
			67.04	4.36	5.59	7.13	

<sup>a</sup> Reaction time 4 h; <sup>b</sup> only washed with ether–cyclohexane mixture; <sup>c</sup> reaction time 2 h.

*Periodide III*: Monoclinic space group  $P2_1/n$ ,  $a = 15.441(1)$ ,  $b = 11.376(1)$ ,  $c = 17.099(2)$  Å,  $\beta = 105.71(1)^\circ$ ,  $V = 2\,891.4(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 2.12$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 4.29$  mm<sup>-1</sup>,  $F(000) = 1\,724$ . The structure was also solved by direct methods and anisotropically refined but by block-diagonal least-squares in five blocks. In this case, hydrogen atoms were localized from  $\Delta\rho$  map and expected geometry. All H-atoms were isotropically refined. A semiempirical correction for absorption<sup>13</sup> was applied.

Data collection and structure refinement parameters for compounds *I* and *III* are listed in Table II, atomic parameters in Table III. Figures 1 and 2 show drawings of molecule *I* and ionic structure *III*. Figures 3 and 4 depict corresponding molecular packings indicating the racemic character of the compounds.

TABLE II  
Data collection and structure refinement parameters

Parameter	<i>I</i>	<i>III</i>
Crystal dimensions, mm	0.80 × 0.60 × 0.50	0.45 × 0.40 × 0.25
Diffractometer and radiation used	Enraf-Nonius CAD4 $\lambda(\text{MoK}\alpha) = 0.71073$ Å	
Scan technique	$\omega/2\theta$	
Temperature	293 K	
No. and $\theta$ range of reflection for lattice parameter refinement	20; 15 – 16°	23; 19 – 21°
Range of $h$ , $k$ and $l$	-14→14, 0→15, -16→16	-16→16, -11→11, 0→18
Standard reflection monitored in interval; intensity fluctuation	120 min; -0.5%	120 min; -2%
Total number of reflections measured; $2\theta$ range	5 975; 0 – 50°	7 502; 0 – 50°
No. of observed reflections	2 181	2 682
Value of $R_{\text{int}}$	0.042	0.023
Criterion for observed reflections	$I \geq 1.96 \sigma(I)$	$I \geq 1.96 \sigma(I)$
Function minimized	$\sum w ( F_o  -  F_c )^2$	
Weighting scheme	$w = [\sigma^2(F_o)]^{-1}$	$w = 1$
Parameters refined	280	411
Value of $R$ , $wR$ and $S$	0.081, 0.062, 1.250	0.025, 0.025, 1.802
Ratio of max. least squares shift to e.s.d. ( $\Delta/\sigma$ ) in the last cycle	0.002	0.002
Max. and min. heights in final $\Delta\rho$ map	0.24, -0.29 e Å <sup>-3</sup>	0.66, -0.54 e Å <sup>-3</sup>
Source of atomic factors	ref. <sup>19</sup>	
Programs used	CRYSTALS (ref. <sup>20</sup> ), SDP (ref. <sup>21</sup> ), SHELXS86 (ref. <sup>22</sup> ), PARST91 (ref. <sup>23</sup> ), SHELX76 (ref. <sup>24</sup> )	
Computers used	PDP 11/73, PC AT 486	

TABLE III

Final coordinates ( $\cdot 10^4$ ) and their equivalent isotropic thermal parameters ( $\cdot 10^3$ ) for non-hydrogen atoms. The isotropic equivalent parameter is defined as  $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i a_j \mathbf{a}_i^* \mathbf{a}_j^*$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
<i>Molecule I</i>				
O1	4737(4)	2659(4)	2483(3)	87(2)
N1	1716(4)	-232(3)	1404(3)	57(2)
N4	884(3)	805(3)	2347(3)	50(2)
C2	2531(4)	223(4)	2086(3)	47(3)
C3	2050(4)	880(4)	2670(3)	47(3)
C5	-6(5)	1322(5)	2623(4)	68(3)
C6	-1071(5)	1134(5)	2163(5)	80(4)
C7	-1277(5)	417(6)	1396(5)	75(4)
C8	-389(5)	-76(5)	1110(4)	68(3)
C9	726(5)	123(4)	1578(4)	53(2)
C10	2522(4)	1582(4)	3461(4)	50(2)
C11	3279(5)	2302(4)	3333(4)	56(2)
C12	3715(5)	2518(4)	2419(4)	62(3)
C13	2147(4)	1429(4)	4400(4)	53(2)
C14	2061(5)	2244(5)	5028(4)	69(3)
C15	1629(5)	2104(5)	5876(4)	74(3)
C16	1286(5)	1154(6)	6114(4)	73(4)
C17	1395(5)	336(5)	5529(4)	71(3)
C18	1806(4)	471(4)	4675(4)	57(3)
C19	2938(5)	2587(4)	1459(4)	57(2)
C20	3385(6)	2431(4)	624(4)	71(3)
C21	2689(7)	2509(5)	-270(5)	84(4)
C22	1561(7)	2752(5)	-355(5)	84(4)
C23	1113(6)	2917(5)	472(5)	82(4)
C24	1791(6)	2824(4)	1371(5)	66(4)
C25	3750(5)	-19(4)	2124(4)	53(2)
C26	4125(5)	-313(5)	1288(4)	74(3)
C27	5244(6)	-577(6)	1310(5)	92(4)
C28	5998(6)	-561(6)	2161(6)	92(4)
C29	5652(5)	-268(5)	3001(5)	82(4)
C30	4529(5)	8(4)	2985(4)	68(3)
<i>Periodide III</i>				
I1	5294(0)	2199(0)	9253(0)	87(1)
I2	8489(0)	1433(0)	174(0)	87(1)
I3	5000	0	10000	60(1)

TABLE III  
(Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
I4	10000	0	0	76(1)
N1	3621(3)	1685(4)	1229(2)	56(2)
N4	3858(3)	3377(4)	719(2)	54(2)
O1	3238(2)	5225(3)	1456(2)	75(2)
C2	4292(3)	2257(5)	1810(3)	50(2)
C3	4427(3)	3322(5)	1513(3)	51(2)
C5	3741(4)	4259(6)	152(4)	67(3)
C6	3126(5)	4098(7)	-575(4)	77(3)
C7	2625(6)	3073(8)	-729(5)	83(4)
C8	2715(4)	2205(7)	-181(4)	70(3)
C9	3367(4)	2378(5)	573(3)	57(2)
C10	5069(3)	4258(4)	1889(3)	48(2)
C11	4808(4)	5324(5)	2055(3)	54(2)
C12	3866(4)	5723(5)	1936(3)	57(2)
C13	6032(3)	3930(4)	2088(3)	51(2)
C14	6680(4)	4490(6)	2713(4)	65(3)
C15	7567(5)	4197(8)	2871(5)	83(3)
C16	7846(5)	3346(7)	2429(5)	89(4)
C17	7224(5)	2785(7)	1818(5)	85(3)
C18	6332(5)	3059(6)	1659(4)	66(3)
C19	3684(3)	6732(4)	2420(3)	49(2)
C20	2875(4)	7324(6)	2166(4)	62(3)
C21	2687(5)	8239(6)	2611(5)	74(3)
C22	3280(5)	8579(6)	3325(4)	76(3)
C23	4070(5)	7970(7)	3572(4)	82(3)
C24	4287(5)	7086(6)	3130(4)	70(3)
C25	4745(3)	1719(5)	2600(3)	52(2)
C26	5159(5)	644(5)	2642(4)	70(3)
C27	5577(5)	139(6)	3388(4)	85(3)
C28	5582(5)	710(7)	4095(4)	80(3)
C29	5181(5)	1789(7)	4047(4)	87(3)
C30	4771(4)	2317(6)	3316(4)	68(3)
C31	3165(6)	598(7)	1339(6)	78(4)

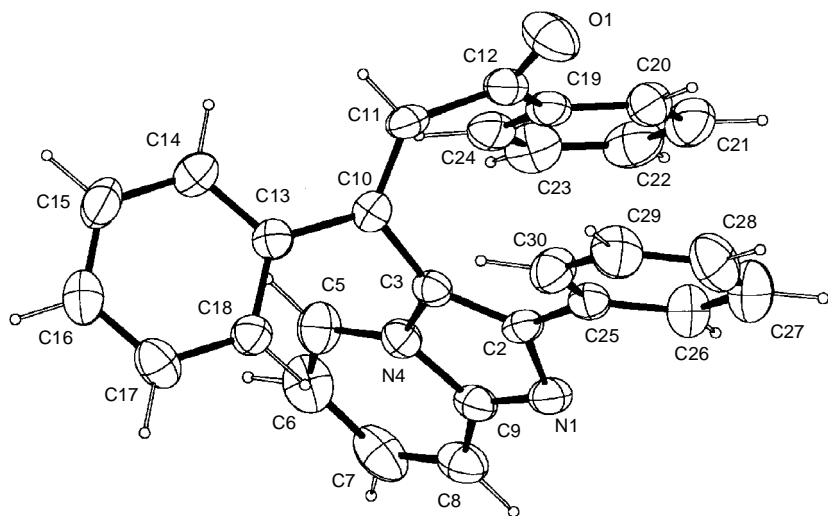


FIG. 1

Molecular structure of heterocyclic base I

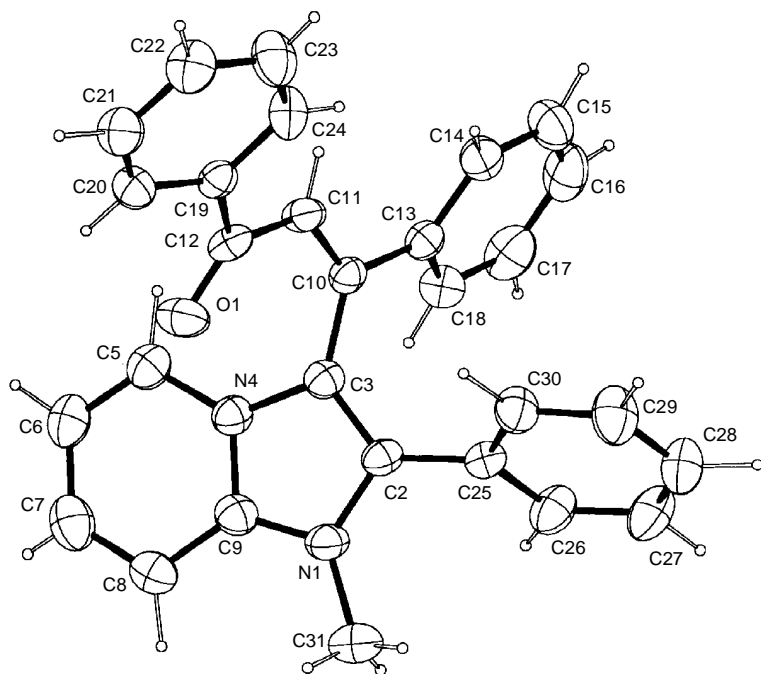


FIG. 2

Molecular structure of heterocyclic cation III

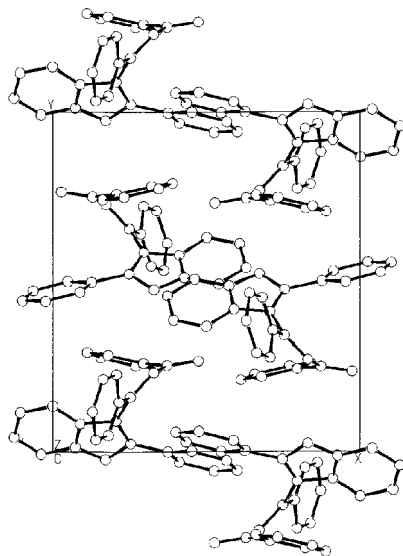


FIG. 3  
Crystal packing of heterocyclic base I

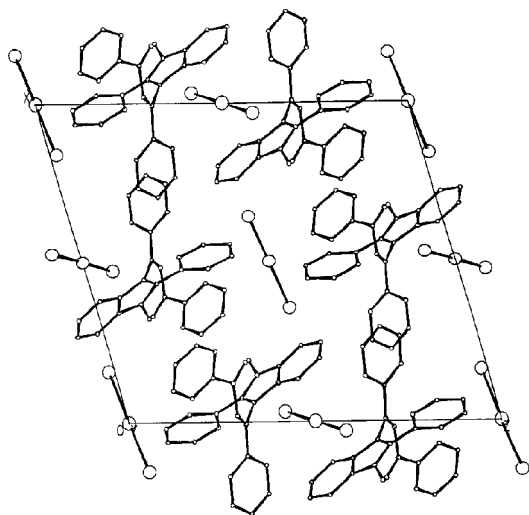


FIG. 4  
Crystal packing of heterocyclic salt III



## Calculations

The geometries and energies of the molecule *I* and protonated cations *VIIIa* – *VIIIc* were calculated and optimized by the standard PM3 method<sup>14</sup>.

## RESULTS AND DISCUSSION

*Crystal and Molecular Structure of Compounds I and III*

The X-ray structures of enone *I* and periodide *III* are shown in Figs 1 and 2. In agreement with the X-ray data of other imidazo[1,2-*a*]pyridine derivatives<sup>7,9,12,15,16</sup>, the heterocyclic systems in *I* and *III* are practically planar and the methyl group in *III* is really at the N1 position. The side chain linkage C=C–CO–Ph adopts, however, different space orientations in the free enone *I* and its quaternary salt *III* as indicated by corresponding C2–C3–C10–C11 dihedral angles, e.g. +55.3 and –118.0°, respectively. The molecular shape of enone *I* resembles to a great extent that of earlier reported<sup>2</sup> aza analogue *II* with the dihedral angle 52.2°. The solid state conformer of salt *III* may be stabilized by an attraction between the carbonyl oxygen O1 and the positively charged heterocyclic system as supported by a significantly shorter distance between the heteroatoms O1 and N4 in periodide *III* cation (2.75 Å) compared with that in free base *I* (5.16 Å). This type of intramolecular interaction has been also associated with possible curariform activities<sup>9</sup>. The usually observed<sup>12</sup> double bond alternation within the linkage C5–C6–C7–C8–C9 in various imidazo[1,2-*a*]pyridines is conserved also in compounds *I* and *III* as follows from bond lengths given in Table IV.

*Solution Structure of Salts III – VII*

The NMR spectra of compounds *I* and *III* – *VII* are of interest showing to which degree the effects of protonation and quaternization of the parent enone *I* may be reflected in the corresponding spectral characteristics. In addition, they provide an information about the N1 regioselectivity in the transformation of base *I* to its salts of expected structures *III* – *VII*.

Complete assignments of <sup>1</sup>H and <sup>13</sup>C NMR spectra of enone *I* and salts *III* – *VII* based on standard 1D and 2D techniques (HOM2DJ, COSY, LR-COSY, HETCOR, LR-HETCOR, APT, coupled C, DEPTGL) are given in Tables V and VI. The proton chemical shifts H-6, H-7 and H-8 of base *I* are similar to those of the parent heterocycle<sup>17</sup> except of the signal of H-5 which is upfield shifted (0.76 ppm) apparently due to anisotropic effects of the side chain at the position 3. The positive charge of cations in quaternary salts *III* – *VI* results not only in deshielding effects at heterocyclic atoms H-5, H-6, H-7, H-8, C-2 and C-3 but also at side chain signals of H-11, C-10 and C-11, thus indicating mutual space vicinities of the molecular counterparts. The NMR patterns of perchlorate *VII* are close to those of quaternary salts *III* – *VI* in agreement with

the expected N1-protonation of base *I* which has been further supported by comparison of the PM3 calculated molecular energies. These have shown the cation *VIIIa* being stabilized by 230.9 and 109.1 kJ mol<sup>-1</sup> with respect to alternatives *VIIIb* and *VIIIc*,

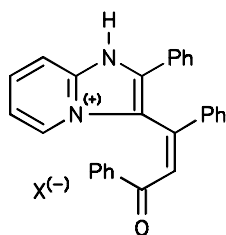
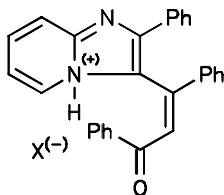
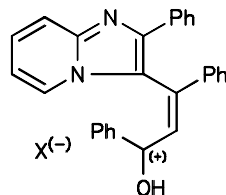
*VIIIa**VIIIb**VIIIc*

TABLE IV

Comparison of some calculated and observed bond lengths (Å) and bond angles (°) for compounds *I* and *III*

Bond	Base <i>I</i>		Periodide <i>III</i>	
	X-ray	PM3	X-ray	PM3 <sup>a</sup>
N1–C2	1.368(6)	1.386	1.388(6)	1.414
C2–C3	1.375(6)	1.407	1.351(8)	1.392
C3–N4	1.386(6)	1.406	1.405(6)	1.414
N4–C5	1.368(6)	1.397	1.373(8)	1.395
C5–C6	1.338(7)	1.367	1.357(8)	1.373
C6–C7	1.410(8)	1.425	1.385(12)	1.421
C7–C8	1.357(8)	1.366	1.342(12)	1.371
C8–C9	1.397(7)	1.422	1.418(8)	1.417
C9–N1	1.330(6)	1.367	1.340(6)	1.397
C9–N4	1.380(6)	1.414	1.351(7)	1.401
C3–C10	1.468(6)	1.459	1.478(7)	1.464
C10–C11	1.335(6)	1.340	1.333(8)	1.341
C11–C12	1.488(7)	1.488	1.484(9)	1.489
C12–O1	1.219(6)	1.215	1.226(6)	1.220
C9–N1–C2	105.4(4)	106.1	108.4(4)	109.1
N1–C2–C3	111.3(5)	110.7	108.2(4)	107.3
C2–C3–C10	133.6(5)	131.1	129.5(5)	128.9
C3–C10–C11	120.9(5)	122.8	122.9(5)	122.9
C11–C12–O1	117.5(5)	122.1	121.2(5)	121.1

<sup>a</sup> The calculation was performed for the counter-cation only.

respectively. It may be additionally noted that the magnetic equivalence observed for *ortho*, *meta* and *para* counter-protons in all studied compounds reflect unrestricted rotations of phenyl residue in the positions 2, 10 and 12 under conditions of the measurement.

### PM3 Calculations of Compounds I and III

The PM3 optimization of molecule *I* and cation *III* gave satisfying bond lengths (Table IV) in main cases and led to molecular shapes similar to those found by the X-ray analysis. Surprisingly, the fit for the cation *III* was found to be even better (Fig. 5) than that for

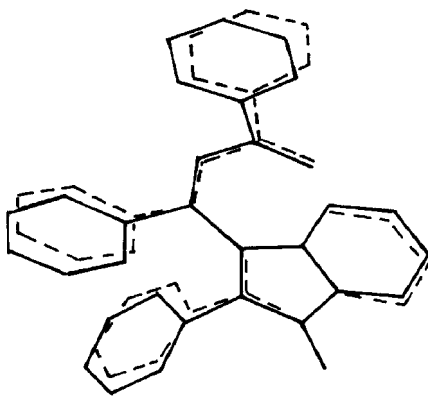


FIG. 5

Comparison of X-ray and PM3 calculated molecular shapes for cation *III*. Dashed parts follow from the theoretical treatment

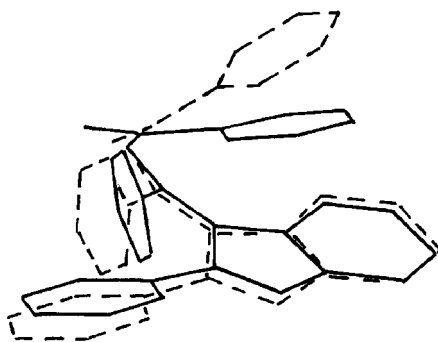


FIG. 6

Comparison of X-ray and PM3 calculated molecular shapes for heterocyclic base *I*. Dashed parts follow from the theoretical treatment

the parent base *I* where the subspace around the benzoyl group is apparently more affected by crystal field effects (Fig. 6). In both cases, however, a different space configuration of the side linkage is correctly interpreted by the semiempirical PM3 method thus independently showing that the species *I* and *III* are chiral at least in the solid state<sup>18</sup>.

TABLE V  
<sup>1</sup>H NMR spectral data ( $\delta$ , ppm) of studied compounds in (CD<sub>3</sub>)<sub>2</sub>SO

Proton	Compound						
	<i>I</i> <sup>a</sup>	<i>II</i>	<i>III</i> <sup>b</sup>	<i>IV</i> <sup>c</sup>	<i>V</i> <sup>d</sup>	<i>VI</i> <sup>e</sup>	<i>VII</i>
H5	7.850	8.378	8.455	8.454	8.485	8.584	8.454
H6	6.854	7.036	7.540	7.545	7.560	7.592	7.44
H7	7.305	8.660	8.161	8.167	8.181	8.170	8.040
H8	7.636	–	8.428	8.442	8.524	8.407	8.083
H11	7.978	8.082	8.22	8.234	8.192	8.24	8.346
<i>o</i> -Ph2	7.685	7.714	7.32	7.343	7.287	7.142	7.44
<i>m</i> -Ph2	7.234	7.249	7.32	7.231	7.335	7.252	7.40
<i>p</i> -Ph2	7.155	7.180	7.36	7.373	7.398	7.356	7.32
<i>o</i> -Ph10	7.507	7.548	7.703	7.734	7.731	7.742	7.772
<i>m</i> -Ph10	7.372	7.357	7.41	7.395	7.404	7.404	7.39
<i>p</i> -Ph10	7.413	7.410	7.46	7.464	7.438	7.447	7.42
<i>o</i> -Ph12	7.826	7.918	7.888	7.896	7.913	7.954	7.957
<i>m</i> -Ph12	7.372	7.428	7.48	7.475	7.472	7.491	7.43
<i>p</i> -Ph12	7.507	7.552	7.64	7.634	7.633	7.656	7.60

<sup>a</sup> Typical coupling constants in Hz:  $J(5,6) = 6.9$ ,  $J(5,7) = 1.0$ ,  $J(5,8) = 1.2$ ,  $J(6,7) = 6.9$ ,  $J(6,8) = 1.2$  and  $J(7,8) = 9.0$ ,  $J(o,m) = 7.2$ ,  $J(m,p) = 7.4$  and  $J(o,p) = 1.4$  for Ph2,  $J(o,m) = J(m,p) = 6.3$  and  $J(o,p) = 1.4$  for Ph10 and  $J(o,m) = J(m,p) = 7.2$  and  $J(o,p) = 1.4$  for Ph12; <sup>b</sup> 3.949 s, 3 H (CH<sub>3</sub>); <sup>c</sup> 3.950 s, 3 H (CH<sub>3</sub>); <sup>d</sup> 1.296 dd, 3 H,  $J = 7.3$  and 7.3 (CH<sub>3</sub>); 4.408 dq, 1 H and 4.456 dq, 1 H  $J = 14.8$  and 7.3 (CH<sub>2</sub>); <sup>e</sup> 5.602 d, 1 H and 5.868 d, 1 H (CH<sub>2</sub>); 6.976 d, 2 H (*o*-Ph) and 7.32 m, 3 H (*m,p*-Ph).

TABLE VI  
 $^{13}\text{C}$  NMR spectral data ( $\delta$ , ppm) of studied compounds in  $(\text{CD}_3)_2\text{SO}$

Carbon	Compound						
	<i>I</i>	<i>II</i>	<i>III</i> <sup>a</sup>	<i>IV</i> <sup>b</sup>	<i>V</i> <sup>c</sup>	<i>VI</i> <sup>d</sup>	<i>VII</i>
C2	117.81	116.51	120.91	120.89	134.54	121.80	119.64
C3	143.01	143.95	135.26	135.53	121.29	134.49	133.24
C5	124.91	133.35	127.28	127.22	127.52	127.73	126.96
C6	112.59	109.90	117.95	117.92	118.03	118.43	117.70
C7	125.39	150.39	133.97	133.92	134.18	134.91	133.88
C8	116.76	–	111.87	111.93	111.78	111.79	112.54
C9	144.69	147.88	139.46	139.48	138.76	139.56	139.92
C10	141.06	140.36	135.96	136.00	135.98	135.91	136.93
C11	128.19	127.88	130.55	130.39	130.36	130.38	130.32
C12	189.82	189.40	189.44	189.94	189.54	189.47	189.50
<i>i</i> -Ph2	133.66	133.10	124.29	124.34	124.37	124.16	126.26
<i>o</i> -Ph2	127.09	127.35	128.89	128.84	129.53	129.47	127.42
<i>m</i> -Ph2	128.24	128.30	129.73	129.73	128.96	128.85	129.31
<i>p</i> -Ph2	127.53	128.01	130.55	130.53	130.63	130.69	131.16
<i>i</i> -Ph10	137.36 <sup>e</sup>	137.22	136.80	136.83	135.51	136.95	136.58 <sup>e</sup>
<i>o</i> -Ph10	127.59	127.79	127.80	127.85	127.85	127.78	127.89
<i>m</i> -Ph10	128.41	129.03	129.08	129.05	129.01	129.06	128.73
<i>p</i> -Ph10	130.39	130.41	130.99	130.96	130.94	131.02	130.41
<i>i</i> -Ph12	137.61 <sup>e</sup>	137.61	135.56	135.50	136.93	135.40	137.07 <sup>e</sup>
<i>o</i> -Ph12	127.97	128.14	128.43	128.43	128.41	128.49	128.42
<i>m</i> -Ph12	129.13	128.52	128.68	128.67	128.63	128.74	129.24
<i>p</i> -Ph12	132.83	133.03	133.64	133.62	133.56	133.71	133.60

<sup>a</sup> 32.42 ( $\text{CH}_3$ ); <sup>b</sup> 32.44 ( $\text{CH}_3$ ); <sup>c</sup> 14.58 ( $\text{CH}_3$ ) and 40.46 ( $\text{CH}_2$ ); <sup>d</sup> 47.88 ( $\text{CH}_2$ ), 121.80 (*i*-Ph), 126.07 (*o*-Ph), 128.05 (*m*-Ph) and 128.83 (*p*-Ph); <sup>e</sup> interchangeable assignments.

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