Nitrenium ions. Part 4.[1] Reactivity and crystal structure of 1-methyl-2-phenyl-3-*N*-benzoyloxyindole iminium perchlorate and reactivity of *N*,*N*-dimethylamino-*p*-*N*-benzoyloxyaniline nitrenium chloride with 2-phenylindole

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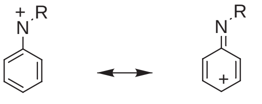
1-Methyl-2-phenyl-3-nitrosoindole and *N*,*N*-dimethyl-*p*-nitrosoaniline react with benzoyl chloride to form salts behaving like iminium and nitrenium ions respectively. The structure of the ion formed in the case of the nitrosoindole was elucidated by X-ray analysis. The charge density distribution of both ions was calculated on the basis of the structure parameters and by AM1 calculations and their reactivity was interpreted on the basis of structural parameters and the calculated distribution of their positive charge.

The chemistry of nitrenium ions, which are characterised by a double bonded positive nitrogen and bear a lone pair, was first reviewed in 1964,[2] and again in 1970[3] and 1973.[4] However, interest in these intermediates was only stimulated by Gassman's review[5] and his work,[6] even though the idea of a positive charged bivalent nitrogen was introduced at the beginning of this century.[7] For many years nitrenium ions were the object of discussion and doubts were expressed as to their existence,[8–10] which was confirmed by subsequent work more recently reviewed by Abramovitch[11] and Russian researchers.[12] In fact, aryl nitrenium ions **1**$^+$ were considered as iminic derivatives with the positive charge localised on the conjugated aromatic ring.[13] This supposition, of course, was supported by the reactivity of these species, which in many cases involves nucleophilic attack at a carbon atom conjugated with the nitrogen.[13–15]



1$^+$

In previous work we also demonstrated that protonated nitroso arenes [eqn. (1)] attack indoles through the nitrogen

$$\mathrm{Ar{-}N{=}O} + \mathrm{H^+} \rightleftharpoons \mathrm{Ar{-}N^+{-}OH} \qquad (1)$$

forming a new carbon–nitrogen bond.[16] The results previously obtained on activating the nitroso arenes with acids[1,16] were also obtained in the presence of benzoyl chloride:[17] in these cases the nitrenium ions should be formed according to eqn. (2).

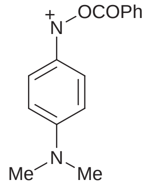
$$\mathrm{Ar{-}N{=}O} + \mathrm{PhCOCl} \rightleftharpoons \mathrm{Ar{-}N^+OCOPh\ Cl^-} \qquad (2)$$

Nitrenium ions have always been considered as intermediates but recently one of them was isolated and its structure elucidated by X-ray analysis.[18] In the present work we describe the crystal structure of compound **3**$^+$, isolated as the iminium perchlorate, and its reactivity with respect to nitrenium ion **2**$^+$.

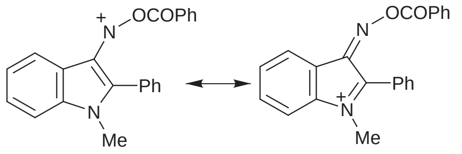
Results and discussion

Structure and reactivity

Nitroso arenes such as nitrosobenzene, *p*-chloronitrosobenzene and *p*-methylnitrosobenzene react with benzoyl chloride giving rise to the equilibrium reported in eqn. (2). Since the solution colour does not substantially differ from the solution colour of nitroso arenes and no evident changes are observed in the UV spectrum of the solution of the two reagents, it can be argued that the equilibrium of eqn. (2) is almost shifted to the left. However, when 2-phenylindole is added to the solution mixture of nitroso arenes–benzoyl chloride, an electrophilic attack of Ar–N$^+$–OCOPh Cl$^-$ at C-3 of the indole nucleus is observed and 2-phenyl-3-(arylimino)-3*H*-indoles were isolated.[17] Similar behaviour was observed when *N*,*N*-dimethyl-*p*-nitrosoaniline was treated with 2-phenylindole in the presence of benzoyl chloride.[17]



2$^+$ Cl$^-$ or ClO$_4^-$



3$^+$ Cl$^-$ or ClO$_4^-$

Since *N*,*N*-dimethyl-*p*-nitrosoaniline with benzoyl chloride leads to the formation of a precipitate with disappearance of the green colour of the nitroso form, we tried, but without success, to isolate the product in crystal form suitable for an X-ray analysis.

The experiments carried out with *N*,*N*-dimethyl-*p*-nitrosoaniline suggested that the equilibrium of eqn. (2) was more

Table 1 Selected bond distances (Å) and angles (°) with esd's in parentheses

Bond distances			
O(31)–N(31)	1.377(11)	N(31)–C(3)	1.272(13)
O(31)–C(31)	1.399(14)	C(2)–C(3)	1.468(14)
O(32)–C(31)	1.193(16)	C(2)–C(21)	1.466(16)
N(1)–C(2)	1.298(15)	C(3)–C(4)	1.443(16)
N(1)–C(9)	1.424(15)	C(4)–C(9)	1.403(14)
N(1)–C(11)	1.464(21)	C(31)–C(32)	1.433(16)
Bond angles			
N(31)–O(31)–C(31)	111.7(8)	N(31)–C(3)–C(2)	118.5(9)
C(2)–N(1)–C(9)	111.2(10)	N(31)–C(3)–C(4)	135.2(11)
C(2)–N(1)–C(11)	127.7(12)	C(2)–C(3)–C(4)	106.2(9)
C(9)–N(1)–C(11)	121.0(11)	C(3)–C(4)–C(9)	106.3(9)
O(31)–N(31)–C(3)	112.1(8)	N(1)–C(9)–C(4)	107.9(9)
N(1)–C(2)–C(3)	108.4(9)	O(31)–C(31)–O(32)	120.4(11)
N(1)–C(2)–C(21)	124.4(11)	O(31)–C(31)–C(32)	111.5(10)
C(3)–C(2)–C(21)	127.2(9)	O(32)–C(31)–C(32)	128.1(11)

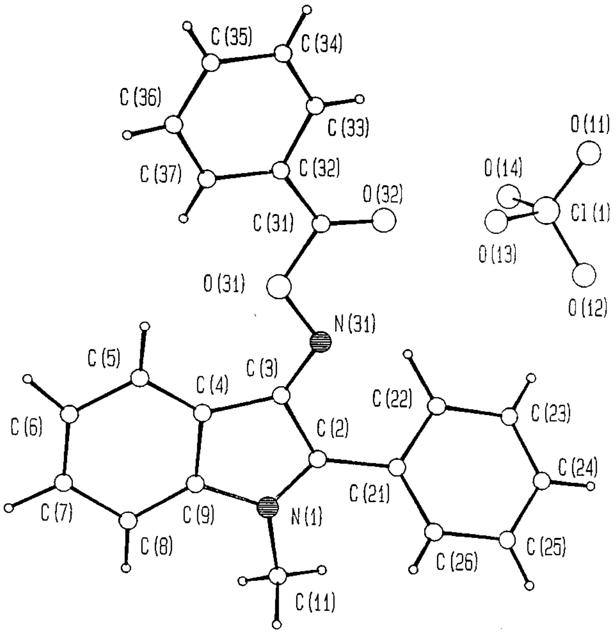
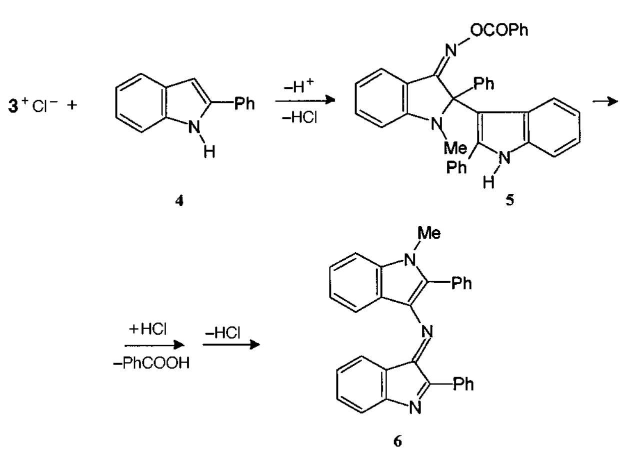


Fig. 1 Perspective view of compound 3^+ ClO_4^-.

shifted to the right in the case of more nucleophilic nitroso compounds. This is the reason why we attempted to isolate the nitrenium ion **3**$^+$ starting from 1-methyl-2-phenyl-3-nitrosoindole in which nitrogen is in a conjugated position with electron donor groups. The chloride salt was first formed by mixing the nitroso derivative with benzoyl chloride, converted into the corresponding perchloride and then crystallised from chloroform–diethyl ether: suitable crystals of **3**$^+$ ClO_4^- were observed for the structure determination (Fig. 1). The bond distance values N(1)–C(2) 1.298, C(2)–C(3) 1.468, C(3)–N(31) 1.272 Å, reported in Table 1, are more consistent with the indolenine mesomeric form than with the nitrenium ion structure (see later).

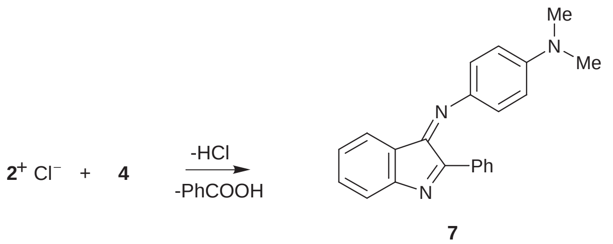
The reactivity of compound **3**$^+$ with 2-phenylindole **4**, chosen as a nucleophile, is also consistent with the indolenine structure; in fact, compound **4** attacks the more hindered C-2 rather than the less crowded exocyclic nitrogen as shown in Scheme 1.

The reaction of **3**$^+$ Cl$^-$ with **4** at first affords adduct **5**, which in the presence of the hydrogen chloride formed undergoes elimination of benzoic acid and migration of the 2-phenylindole moiety from C-2 to the exocyclic nitrogen forming compound **6**. The reaction sequence was demonstrated by treating pure adduct **5** with hydrogen chloride in the same reaction solvent.[19] In the reaction of **3**$^+$ Cl$^-$ with **4** previously described[20] the adduct **5** was never isolated; adducts of this kind were only isolated with 1-alkyl-2-phenylindole.[21] Ion **3**$^+$ undergoing nucleophilic attack at C-2 behaves like diarylnitrenium ions when they react with electron rich alkenes as recently described.[22]



Scheme 1

N,*N*-Dimethyl-*p*-nitrosoaniline with benzoyl chloride affords nitrenium ion **2**$^+$ Cl$^-$, which reacts with **4** to form 2-phenyl-3-(*p*-dimethyliminophenyl)-3*H*-indole **7** as shown in Scheme 2, as has been previously observed.[23]



Scheme 2

In this case, adducts involving the indole nucleophilic attack on the nuclear carbon of **2**$^+$ Cl$^-$ were never observed; thus, the nucleophilic attack of 2-phenylindole **4** occurs directly on the exocyclic nitrogen, supporting in some way that the nitrenium form is the predominant one among those of its mesomeric system. The failure to attain suitable crystals for an X-ray analysis of **2**$^+$ ClO_4^- prevents a complete understanding of its reactivity.

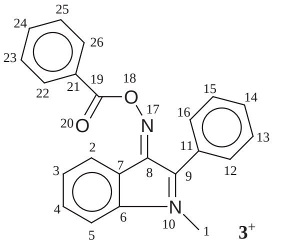
In order to obtain more information on the reactivity of **2**$^+$ and **3**$^+$ towards nucleophiles, we performed semiempirical calculations to evaluate the positive charge distribution in both cases.

AM1 calculations on 2$^+$ and 3$^+$

The positive charge distributions in **2**$^+$ and **3**$^+$ were calculated by using the quantomechanical AM1 method[24] and the results are reported in Table 2(a) and 2(b). In order to predict the nucleophilic site of attack, the most positive charged sites must be known.[25] The values obtained demonstrate that the most positive position in ion **3**$^+$ is C-2 [C9 in Table 2(a)] in agreement with our results. On the other hand, the charge distribution in ion **2**$^+$ shows that one of the most positive positions is the exocyclic nitrogen [N8 in Table 2(b)] and this could explain the experimental results observed for ion **2**$^+$, which really seems to behave as a nitrenium ion. The frontier molecular orbital electron density gives better insights into the charge density distribution. The values of f_r^N (nucleophilic electron density) calculated by the same method better highlight the distribution of the positive charge in salts **2**$^+$ and **3**$^+$, according to the literature reports.[26,27]

Table 2 Charge density and nucleophilic electron density distribution on salts $\mathbf{3}^+$ (a) and $\mathbf{2}^+$ (b)

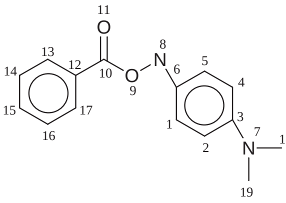
(a)



$\mathbf{3}^+$

Position on molecule	$Q_{\text{A net charge}}$	f_r^N LUMO
C1	−0.1218	1.35 10^{-4}
C2	−0.0569	1.18 10^{-3}
C3	−0.09381	3.15 10^{-2}
C4	−0.0996	3.14 10^{-3}
C5	−0.0836	3.27 10^{-2}
C6	−0.0513	1.43 10^{-2}
C7	−0.04647	3.00 10^{-2}
C8	−0.1021	1.30 10^{-2}
C9	0.2252	0.374
N10	−0.0457	0.151
N17	0.150	0.178
O18	−0.2394	2.96 10^{-2}
C19	0.3868	4.49 10^{-3}
O20	−0.2302	5.02 10^{-3}

(b)



$\mathbf{2}^+$

Position on molecule	$Q_{\text{A net charge}}$	f_r^N LUMO
C1	0.0150	0.150
C2	−0.2281	1.66 10^{-2}
C3	0.2310	0.240
C4	−0.2431	1.16 10^{-2}
C5	0.0573	0.148
C6	−0.1689	7.18 10^{-3}
N7	−0.1485	0.126
N8	0.1729	0.223
O9	−0.2383	4.41 10^{-2}
C10	0.3937	5.05 10^{-3}
O11	−0.2194	6.32 10^{-3}

Molecular geometry of 1-methyl-2-phenyl-3-*N*-benzoyloxyindole iminium perchlorate $\mathbf{3}^+$ ClO_4^-

Selected bond distances and angles are given in Table 1 and the arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1, which represents a perspective view of the molecule.

The intramolecular bond lengths and angles, in line with the hybridisation expected for the atoms involved and in reasonable agreement with those of analogous compounds reported in the literature,[16,28] show in particular the presence of three localised double bonds: N(1)=C(2) 1.298(15) Å showing the iminium ion character of the nitrogen in the pyrrolic ring, N(31)=C(3) 1.272(13) Å confirming the iminic form of the N(31) atom and C(31)=O(32) 1.193(16) Å as expected for the carbonyl group in the benzoyloxy moiety. Moreover the sequence of short N(1)=C(2), long C(2)–C(3) 1.468(14) Å and short C(3)=N(31) distances and the planar geometry of this part of the molecule [torsion angle N(1)=C(2)–C(3)=N(31) 0.9(9)°] suggest the possibility of a conjugate interaction between the p orbital of the N(1) and N(31) atoms.

From the study of the molecular conformation, three planar moieties are found in the molecule: the indole nucleus [*A*], the benzoyloxy moiety [*B*] and the benzene in position 2 [*C*]. The analysis of the planarity indicates that the dihedral angles they form are [*A*]^[*B*] 12.3(2), [*A*]^[*C*] 37.9(3) and [*B*]^[*C*] 38.5(3)°, the C(31)–O(31)–N/31=C(3) torsion angle being 8.6(8)°.

The perchlorate ion has the geometry expected and is not in contact with the organic cation. Packing is consistent with van der Waals interactions.

Conclusions

On the basis of the experimental data concerning the reactivity of nitroso arenes with nucleophiles in the presence of benzoyl chloride, the results of the X-ray analysis and the calculations performed on the positive charge distribution, it may be concluded that: (i) nitroso arenes can be activated to the corresponding nitrenium ions by benzoyl chloride; (ii) the positive charge of the nitrenium ion formed is delocalised on the conjugated π-system; (iii) the equilibrium of eqn. (2) is more shifted to the right when the nitroso group is in a conjugated position with electron donor groups; (iv) aryl nitrenium ions may undergo nucleophilic attack on the positive nitrogen as well as on a conjugated carbon depending on the structure of the nitroso derivative.

Experimental

Melting points were measured on an electrothermal apparatus and are uncorrected. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 298 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer. Chemical shifts are given in ppm and *J* values in Hz. Mass spectra were recorded in EI$^+$ mode on a Carlo Erba QMD 1000 GC–MS spectrometer, equipped with a direct probe apparatus. *N*,*N*-Dimethyl-*p*-nitrosoaniline, 2-phenylindole, 1-methyl-2-phenylindole and benzoyl chloride (freshly distilled) were Aldrich commercial compounds. 1-Methyl-2-phenyl-3-nitrosoindole was prepared according to the literature reports.[29]

Synthesis of 3^+ ClO_4^-

1 mmol (236 mg) of 1-methyl-2-phenyl-3-nitrosoindole was dissolved in 40 ml of acetonitrile and then 1.5 mmol (210 mg) of benzoyl chloride were added under stirring at room temperature: the colour of the solution changed over time from green to yellow–orange. After 10 min a solution of 2 mmol (245 mg) of $NaClO_4$ in 10 ml of CH_2Cl_2 was added dropwise to the reaction mixture and a red precipitate began to form immediately.

The reaction mixture was stirred for 1 h and then the precipitate was filtered off and crystallised from acetonitrile–diethyl ether.

Compound $\mathbf{3^+\ ClO_4^-}$: Yield: 80%; mp 219 °C; ^{1}H NMR (200 MHz, DMSO, 25 °C, TMS): $\delta = 3.96$ (s, 3H, CH_3), 7.30 (s-br, 2H, Ph), 7.47–7.57 (m, 5H, Ph), 7.60–7.76 (m, 5H, Ph), 7.94–7.98 (d-br, 2H, Ph); IR (Nujol): $\nu = 1760$ (C=O) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 341 (10) [$M^+ - ClO_4$], 264 (23) [$M^+ - ClO_4 - C_6H_5$], 236 (34) [$M^+ - ClO_4 - C_6H_5{-}CO$], 55 (100); $C_{22}H_{17}N_2O_6Cl$ (440.8).

Reactions of 2^+ Cl^- with 2-phenylindole

The adduct $\mathbf{2}^+$ Cl^- was prepared *in situ* by dissolving 0.5 mmol (75 mg) of *N*,*N*-dimethyl-*p*-nitrosoaniline in 20 ml of acetonitrile followed by addition under stirring of 0.5 mmol (70 mg) of benzoyl chloride: the green solution became yellow and a precipitate of the same colour, corresponding to adduct $\mathbf{2}^+$ Cl^-, began to form.

Table 3 Experimental data for the X-ray diffraction studies on crystalline compound 3^+ ClO_4^-

Formula	$C_{22}H_{17}N_2O_6^+ClO_4^-$
Cryst. habit	Tabular prism
Cryst. colour	Pale yellow
FW *F*(000)	440.8 912
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
Cell parameters at 295 K[a]	
a/Å	8.294(2)
b/Å	16.409(3)
c/Å	15.128(3)
α/°	90
β/°	101.1(1)
γ/°	90
V/Å^3	2020.4(10)
Z	4
d_{calc}/g cm^{-3}	1.45
Cryst. dimens./mm	0.09, 0.24, 0.47
Linear abs. coeff./cm^{-1}	20.6
Diffractometer	Siemens AED
Scan type	ω–2θ
Scan width/deg	[b]
Radiation	[c]
2 range collcn./deg	6–140
hkl range	±*h*, *k*, *l*
Unique total data	4111
Criterion of obsn.	$I > 2\sigma(I)$
Unique obs. data (NO)	1180
No. of refined par. (NV)	280
Overdetermination ratio (NO/NV)	4.2
Absorption	[d]
Solution	[e]
H atoms	[f]
R	0.056
R_w	0.058
GOF	1.3
Largest shift/esd	0.6
Largest peak/e Å^{-3}	0.3
Computer and programs	[g]

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centred reflections chosen from diverse regions of reciprocal space. [b] From $(\theta - 0.6)°$ to $[\theta + (0.6 + \Delta\theta)]°$; $\Delta\theta = [(\lambda a_2 - \lambda a_1)/\lambda]\tan\theta$. [c] Ni-filtered CuK$\alpha\lambda$ = 1.54178 Å. [d] No correction applied. [e] Direct methods. [f] Introduced in the final structure factors in calculated position. [g] ENCORE e91, SHELXS86,[30] SHELX76,[31] PARST.[32] $R = \Sigma|\Delta F|/\Sigma|F_o|$; $R_w = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$; $\mathrm{GOF} = [\Sigma w|\Delta F|^2/(\mathrm{NO} - \mathrm{NV})]^{\frac{1}{2}}$.

The reaction mixture was cooled to 5 °C, then 0.5 mmol (97 mg) of 2-phenylindole were added under stirring and the colour of the solution changed from yellow to dark-green immediately. After 3 h the reaction mixture was evaporated to a small volume and 20 ml of anhydrous diethyl ether were added in order to obtain compound **7** as a precipitate.

Compound **7**: Yield: 57%; mp 189 °C; ^{1}H NMR (200 MHz, DMSO, 25 °C, TMS): δ = 3.22 (s, 6H, 2CH$_3$), 7.10 (d, *J* = 8.2, 2H, Ph), 7.20 (t, *J* = 7.4, 2H, Ph), 7.50 (m, 7H, Ph), 8.25 (m, 2H, Ph); IR (Nujol): *ν* = 1600 (C=N) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 326 (6) [M^+ + 1], 325 (8) [M^+], 206 (10) [indole-H], 129 (20) [indole-C$_6$H$_5$], 69 (100); $C_{22}H_{19}N_3$ (325.4).

Reactions of 3^+ Cl^- with 2-phenylindole

0.5 mmol (97 mg) of phenylindole were added under stirring to a solution of 0.5 mmol (188 mg) of the adduct 1-methyl-2-phenyl-3-*N*-benzoyloxyindole iminium chloride 3^+ Cl^- in 20 ml of acetonitrile cooled to 4 °C. The colour of the reaction mixture changed over time from yellow to orange–brown and after a few minutes a yellow precipitate began to form. After 3 h this precipitate, corresponding to compound **5**, was filtered off and crystallised from benzene–petroleum ether. Since the filtrate contained an adequate amount of compound **6**, it was treated with 10% aqueous NaHCO$_3$ and extracted with CH$_2$Cl$_2$. The organic layer was separated, dried on Na$_2$SO$_4$ and evaporated to dryness. The residue, taken up with benzene, was chromatographed on a silica gel column eluting with cyclohexane–ethyl acetate 8:2: in this way a blue–violet fraction corresponding to compound **6** was isolated (its analysis and spectroscopic data are reported below).

Compound **5**: Yield: 38%; mp 157 °C; ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.78 (s, 3H, CH$_3$), 6.53 (d, *J* = 8.3, 1H, Ph), 6.62 (td, *J* = 7.7, *J* = 1.0, 1H, Ph), 6.72 (d, *J* = 8.1, 1H, Ph), 6.91 (ddd, *J* = 8.1, *J* = 7.0, *J* = 1.0, 1H, Ph), 7.02 (m, 2H, Ph), 7.14 (m, 4H, Ph), 7.25 (m, 2H, Ph), 7.36 (m, 4H, Ph), 7.46 (m, 3H, Ph), 7.58 (m, 1H, Ph), 7.76 (dd, *J* = 7.9, *J* = 1.0, 1H, Ph), 7.94 (m, 2H, Ph), 8.24 (br-s, 1H, NH); IR (Nujol): *ν* = 3300 (N–H, br), 1720 (C=O benz.), 1600 (C=N) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 411 (54) [M^+ − benzoic acid], 308 (100), 77 (44) [C$_6$H$_5$]; $C_{36}H_{27}N_3O_2$ (533.7).

Hydrogen chloride catalysed rearrangement of compound 5 to compound 6

A stream of gaseous HCl was bubbled through 200 mg of compound **5** dissolved in the minimum amount of CHCl$_3$ for 1 h. After standing for 12 h the green solution was evaporated to dryness; the residue was taken up with CH$_3$CN and washed with diethyl ether and benzene and then with absolute ethyl alcohol. Crystallisation from CHCl$_3$–Et$_2$O gave compound **6**.

Compound **6**: Yield: 45%; mp 146 °C; ^{1}H NMR (200 MHz, DMSO, 25 °C, TMS): δ = 3.95 (s, 3H, CH$_3$), 6.77 (d, *J* = 7.0, 1H, Ph), 6.93 (d, *J* = 8.0, 1H, Ph), 7.09 (td, *J* = 8.4, *J* = 1.0, 1H, Ph), 7.50 (m, 11H, Ph), 7.77 (d, *J* = 8.2, 1H, Ph), 8.29 (m, 2H, Ph); IR (Nujol): *ν* = 1580 (C=N) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 411 (100) [M^+], 307 (89), 205 (27) [C$_{15}$H$_{11}$N]; $C_{29}H_{21}N_3$ (411.5).

Crystal structure of 1-methyl-2-phenyl-3-*N*-benzoyloxyindole iminium perchlorate 3^+ ClO_4^-

Table 3 shows the experimental and crystallographic data. The intensities I_{hkl} were determined by analysing the reflection profiles by the method of Lehmann and Larsen.[33] Corrections for Lorentz and polarisation effects were performed. Atomic scattering factors were from the International Tables for X-ray Crystallography.[34] Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.†

AM1 calculations

All the calculations were performed by using the semiempirical quantum-mechanical method AM1 enclosed in the software package HyperChem 4.5.[35] First of all, structures 2^+ and 3^+ were optimised and a conformational search performed, varying all the rateable bonds present in the molecules and always using the AM1 Hamiltonian and a statistical algorithm. A scheme introduced in the Monte Carlo Multiple Minimum, or MCMM, method[27] called *usage directed* was in fact used. It seeks to uniformly sample low-energy regions by cycling through all previously accepted conformations when selecting each initial structure. Then the charge distribution was calculated on the low energy conformations of these compounds. AM1 uses Mulliken atomic charges, which are commonly used in Molecular Orbital Theory to predict chemical reactivity.

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† Full crystallographic details, excluding structure factor tables, 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*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/145.

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