Acta Cryst. (1996). B**52**, 823–837

Bond Length–Bond Order Relations and Calculated Geometries for Some Benzenoid Aromatics, Including Phenanthridine. Structures of 5,6-Dimethylphenanthridinium Triflate, [*N*-(6-Phenanthridinylmethyl)-aza-18-crown-6-$\kappa^5O,O',O'',O''',O''''$](picrate-$\kappa^2O,O'$)potassium, and [*N*,*N*′-Bis(6-phenanthridinyl-κN-methyl)-7,16-diaza-18-crown-6-κ^4O,O',O'',O''']sodium Iodide Dichloromethane Solvate

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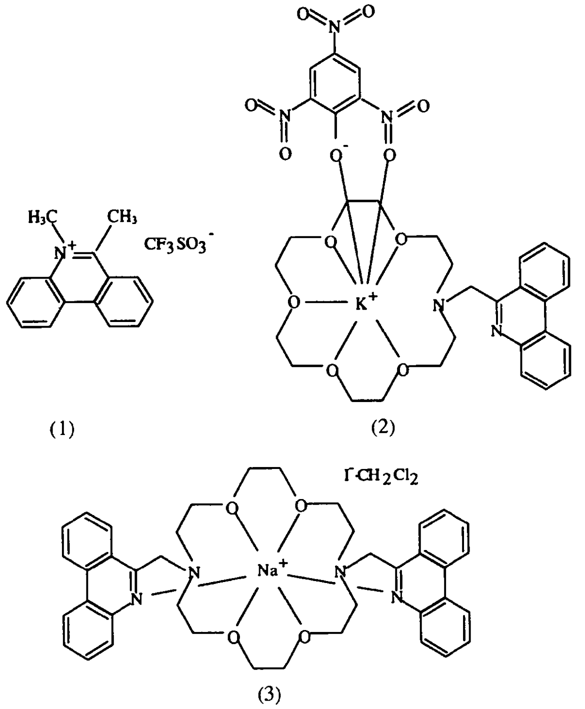
(*Received 19 March 1996; accepted 11 June 1996*)

Abstract

The crystal structures of the title compounds are studied in order to investigate the role of novel fluoroionophores in complexation of sodium and potassium. In the potassium complex seven coordination, including the picrate ligand, is encountered. An additional coordination site is *via* the phenanthridine nitrogen at 3.252 (2) Å (second coordination). The complex is of C_1 symmetry and the aza-18-crown-6 macrocylic ring exhibits a *crown*-type conformation. The 7,16-diaza-18-crown-6 macrocycle accommodates a six-coordinate sodium with two additional ligands, *via* nitrogen from phenanthridine units. The complex cation shows a crystallographic twofold symmetry. The macrocycle is not of the *crown*-type conformation. In both complexes the alkali metals are shifted out of the cavity centres towards a picrate ligand in [*N*-(6-phenanthridinylmethyl)-aza-18-crown-6-$\kappa^5O,O',O'',O''',O''''$](picrate-$\kappa^2O,O'$)-potassium and the phenanthridine units in [*N*,*N*′-bis-(6-phenanthridinyl-κN-methyl)-7,16-diaza-18-crown-6-κ^4O,O',O'',O''']sodium iodide dichloromethane solvate. Semi-empirical and molecular mechanics calculations based on various force fields were used for the optimization of phenanthridine geometry. The values obtained are compared with experimental data. Valence bond calculations of bond lengths in some benzenoid aromatic systems (C—C bonds in benzenoid hydrocarbons, azabenzenoid hydrocarbons and picrate-like systems; C—N bonds in the azabenzenoids; C—O bonds in the picrate-like systems), as well as some analogous Hückel molecular orbital calculations (C—C bonds in the benzenoid hydrocarbons and the azabenzenoids), were found to agree with the observed values (average differences up to 0.015 Å). These approaches can be used by means of bond length–bond order relations for prediction of bond lengths in the phenanthridine units as well as in the picrate.

1. Introduction

The designed attachment of fluorophoric units to crown ethers gives fluoroionophores, the molecules capable of converting the cation recognition process into a specific fluorescence response (Bourson, Pouget & Valeur, 1993; Fages *et al.*, 1990; Morimoto, Fukui, Kawasaki, Iyoda & Shimidzu, 1991). This is the basis for development of sensor molecules for metal cations of interest for analytical purposes, especially in biology and medicine (Minta & Tsien, 1989). The present analysis includes substitued phenanthridine unit (1) and metal complexes with phenanthridine as a ligand in (2) and (3) (Scheme I).



(1)

(2)

(3)

Scheme I. Chemical diagrams of solved structures.

We have recently shown that fluoroionophores (2) and (3), bearing phenanthridine units as pendant arms on the aza-crown, form stable complexes with Na and K picrates (Alihodžić *et al.*, 1993). In addition to donors from the crown ring, the metal cation in such complexes also uses the phenanthridine *N*-donors resulting for (3) by stacking phenanthridine units and the

Table 1. *Experimental details*

Crystal data			
Chemical formula	$C_{15}H_{14}N^+.CF_3SO_3^-$	$C_{32}H_{36}KN_5O_{12}$	$C_{40}H_{44}N_4O_4Na^+.I^-.CH_2Cl_2$
Chemical formula weight	357.36	721.76	879.64
Cell setting	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$I222$
a (Å)	6.816 (1)	9.189 (1)	10.453 (1)
b (Å)	23.687 (3)	11.786 (2)	13.417 (1)
c (Å)	9.966 (2)	15.805 (2)	28.526 (2)
α (°)		83.39 (1)	
β (°)	106.63 (2)	88.29 (1)	
γ (°)		75.78 (1)	
V (Å^3)	1541.6 (5)	1648.2 (4)	4000.6 (5)
Z	4	2	4
D_x (Mg m^{-3})	1.540	1.455	1.460
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	1.54184	0.71073
No. of reflections for cell parameters	25	25	25
θ range (°)	10–19	21–30	18–22
μ (mm^{-1})	0.24	0.20	0.98
Temperature (K)	295 (3)	295 (3)	100 (3)
Crystal form	Prism	Plate	Prism
Crystal size (mm)	0.36 × 0.18 × 0.18	0.29 × 0.11 × 0.05	0.36 × 0.17 × 0.11
Crystal colour	Colourless	Colourless	Yellow
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	ψ scan (North, Phillips & Mathews, 1968)
$T_{\min}$			0.9493
$T_{\max}$			0.9998
No. of measured reflections	3471	7501	2286
No. of independent reflections	2405	4502	2126
No. of observed reflections	1663	3346	1948
Criterion for observed reflections	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 2\sigma(F)$
$R_{\rm int}$	0.0223	0.0167	<0.01
$\theta_{\max}$ (°)	26	74	26
Range of h, k, l	$-8 \rightarrow h \rightarrow 0$ $0 \rightarrow k \rightarrow 29$ $-12 \rightarrow l \rightarrow 12$	$0 \rightarrow h \rightarrow 11$ $-14 \rightarrow k \rightarrow 14$ $-19 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 16$ $-35 \rightarrow l \rightarrow 0$
No. of standard reflections	3	3	3
Frequency of standard reflections	180 min	180 min	Every 57 reflections
Intensity decay (%)	2.4	1.7	1.2
Refinement			
Refinement on	F	F	F
R	0.048	0.040	0.049
wR	0.056	0.040	0.051
S	0.84	0.73	4.24
No. of reflections used in refinement	1663	3346	1948
No. of parameters used	240	565	266
H-atom treatment	All H-atom parameters refined, except only U's refined for H10, H30, H90; H511, H512, H513, H611, H612 and H613 not refined	All H-atom parameters refined, except only U's refined for H10, H20, H23, H25, H30, H40, H70, H80, H90 and H100	H55 all parameters refined; for rest, only U's refined, except H21, H30, H61, H62, H70, H80 and H91 not refined
Weighting scheme	$w = 0.8752/[\sigma^2(F_o) + 0.00232(F_o^2)]$	$w = 1.6721/[\sigma^2(F_o) + 0.00032(F_o^2)]$	$w = 2.7906/[\sigma^2(F_o) + 0.00026(F_o^2)]$
$(\Delta/\sigma)_{\max}$	<0.05	<0.05	<0.05
$\Delta\rho_{\max}$ (e Å^{-3})	0.26	0.41	1.10
$\Delta\rho_{\min}$ (e Å^{-3})	−0.34	−0.30	−1.20
Extinction method	None	None	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)
Computer programs			
Data collection	*EXPRESS CAD-4 software* (Enraf–Nonius, 1989)	*EXPRESS CAD-4 software* (Enraf–Nonius, 1989)	*EXPRESS CAD-4 software* (Enraf–Nonius, 1989)
Cell refinement	*CAD-4 software* (Enraf–Nonius, 1989) *CELDIM* routine	*CAD-4 software* (Enraf–Nonius, 1989) *CELDIM* routine	*CAD-4 software* (Enraf–Nonius, 1989) *CELDIM* routine
Data reduction	*SDP* (B. A. Frenz & Associates, 1982)	*SDP* (B. A. Frenz & Associates, 1982)	*SDP* (B. A. Frenz & Associates, 1982)
Structure solution	*SHELXS86* (Sheldrick, 1985)	*SHELXS86* (Sheldrick, 1985)	*SHELXS86* (Sheldrick, 1985)
Structure refinement	*SHELX76* (Sheldrick, 1976)	*SHELX76* (Sheldrick, 1976)	*SHELX76* (Sheldrick, 1976)
Preparation of material for publication	*PLATON* (Spek, 1982)	*PLATON93* (Spek, 1982)	*PLATON93* (Spek, 1993)

formation of a complex of pseudocriptate structure. The participation of phenanthridine *N*-donors in binding cations may influence both the geometry and bond length–bond order relation. Therefore, the comparative X-ray structural and theoretical studies of (2) and (3) metal complexes and some benzenoid aromatics including phenanthridine have been undertaken in order to compare the phenanthridine geometry and bond lengths obtained from the experimental and theoretical studies. The relations between carbon–carbon bond lengths and Pauling bond orders have been used for many years (Herndon, 1974; Herndon & Párkányi, 1976; Pauling, 1980). The new version of the Cambridge Structural Database (1995, October Release) contains a larger number of structures which have been determined more accurately and these data can be used for more precise derivation of bond length–bond order relationships, including the C—C bonds of benzenoid hydrocarbons, C—C and C—N bonds of benzenoid azahydrocarbons, and C—C and C—O bonds of picrate-like systems. An analogous treatment of the C—C bonds in the benzenoid hydrocarbons and azahydrocarbons using Coulson bond orders (Coulson, 1939) is also possible. In this work these relations are used to predict the bond length character of the aromatic systems present, namely, the phenanthridine units in (1)–(3) (Scheme I) and the picrate in (2). The evaluation of bond lengths in phenanthridine based on computational chemistry methods is also included.

2. Experimental

Crystal data including data collection parameters and details of the structure refinements are listed in Table 1. Crystals were grown at room temperature (1 and 2) from solvent mixtures: 1,2-dichloroethane/dichloromethane for (1), ethylacetate/ethanol for (2), and dichloromethane/diethylether for (3) (at 277 K). Data were rescaled for decay on the basis of intensity reduction of standard reflections. The crystals of (3) were sensitive to light and unstable at room temperature. Data collection for (3) was at 100 K in the dark. Lorentz and polarization corrections were applied using an Enraf–Nonius *SDP* package (B. A. Frenz & Associates, Inc., 1982). For (3) diffractometer software selected the orthorhombic primitive lattice and software for data reduction recommended space group *Pnnn*. A check on crystal symmetry from Weissenberg photographs revealed the space group *I*222, which was confirmed by successful refinement. The *MISSYM* routine [part of the program *PLATON*93 (Spek, 1993*a*)] described by Le Page (1988) accepted this symmetry as correct. Structures (1) and (2) were solved by the direct methods included in *SHELXS*86 (Sheldrick, 1985). The partial structure of (3) was obtained by Patterson's method using *SHELXS*86 (Sheldrick, 1985). Special positions on twofold axes are occupied by sodium (00*z*), iodine (0*y*0) and C55 of the solvent molecule (*x*00). The full-matrix refinement on *F* values minimizing $\sum w(|F_o| - |F_c|)^2$ was used (Sheldrick, 1976). Non-H atoms were refined anisotropically; details of the refinement procedures are listed in Table 1. The correct enantiomer of (3) was selected on the basis of the lower *R* factor. The molecular geometry was calculated by the program package *PLATON*93 (Spek, 1993*a*). Drawings were prepared by *PLUTON*93 (Spek, 1993*b*) and *ORTEP*II (Johnson, 1976). The final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 2, 3 and 4.* In (3) the antiparallel phenanthridine units *syn*-positioned at a short distance of 3.46 (1) Å might explain the pronounced displacements of the atoms affected by the overcrowding. The calculations were performed on the Silicon Graphics workstation of the X-ray Laboratory, Rudjer Bošković Institute, Zagreb, Croatia.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
N50	0.4262 (6)	0.14479 (15)	0.8782 (3)	0.0553 (12)
C10	0.3009 (8)	−0.00098 (18)	0.7427 (5)	0.0606 (16)
C20	0.4856 (9)	−0.0275 (2)	0.7956 (5)	0.0657 (19)
C30	0.6537 (8)	0.0026 (2)	0.8757 (5)	0.0634 (17)
C40	0.6364 (7)	0.0580 (2)	0.9025 (5)	0.0563 (17)
C40*A*	0.4472 (6)	0.08656 (15)	0.8506 (4)	0.0432 (14)
C51	0.6095 (7)	0.17636 (19)	0.9654 (5)	0.0643 (17)
C60	0.2498 (5)	0.17156 (14)	0.8298 (3)	0.0313 (10)
C60*A*	0.0739 (6)	0.14351 (15)	0.7477 (3)	0.0422 (12)
C61	0.2354 (7)	0.23249 (17)	0.8630 (5)	0.0612 (16)
C70	−0.1125 (7)	0.17304 (19)	0.6939 (4)	0.0528 (16)
C80	−0.2813 (7)	0.1462 (2)	0.6137 (5)	0.0592 (17)
C90	−0.2726 (7)	0.0892 (2)	0.5833 (5)	0.0668 (19)
C100	−0.0937 (7)	0.0594 (2)	0.6343 (4)	0.0573 (16)
C10*A*0	0.0835 (6)	0.08566 (16)	0.7158 (4)	0.0433 (11)
C10*B*0	0.2754 (6)	0.05654 (16)	0.7698 (4)	0.0456 (14)
S	0.16894 (16)	0.16675 (4)	0.19221 (11)	0.0481 (3)
F1	0.2018 (5)	0.08929 (11)	0.3848 (3)	0.0870 (11)
F2	−0.0856 (4)	0.13303 (12)	0.3258 (3)	0.0866 (14)
F3	0.1798 (5)	0.17355 (13)	0.4551 (3)	0.0926 (13)
O2	0.0569 (5)	0.21872 (12)	0.1682 (3)	0.0680 (11)
O3	0.3870 (5)	0.17222 (14)	0.2354 (4)	0.0766 (14)
O5	0.0914 (5)	0.12427 (13)	0.0893 (3)	0.0710 (11)
C	0.1141 (7)	0.13893 (18)	0.3452 (5)	0.0555 (17)

3. Molecular and crystal structures

Selected interatomic distances, bond and torsion angles for (1)–(3) are listed in Tables 5, 6 and 7. The molecular structures are shown in Figs. 1–3.

3.1. *Phenanthridine units*

In phenanthridine the free electron pair of nitrogen does not participate in delocalization. Thus, phenanthri-

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* Lists of atomic coordinates, anisotropic displacement parameters, structure factors and refcodes of substances used for analysis have been deposited with the IUCr (Reference: NA0076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

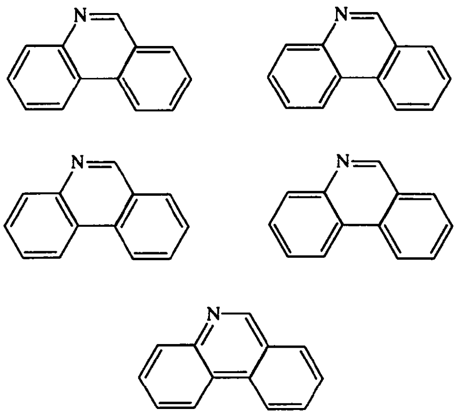
	x	y	z	U_{eq}
K	0.66454 (7)	0.77173 (6)	0.22013 (4)	0.0450 (2)
O	0.9146 (3)	0.59932 (19)	0.17869 (14)	0.0589 (8)
O1	0.3504 (2)	0.76831 (18)	0.23060 (13)	0.0486 (8)
O4	0.5631 (2)	0.60850 (17)	0.33743 (13)	0.0438 (8)
O10	0.9041 (2)	0.86239 (18)	0.27659 (13)	0.0451 (8)
O13	0.6814 (3)	1.02261 (18)	0.17321 (12)	0.0498 (8)
O16	0.4331 (2)	0.95000 (19)	0.12039 (13)	0.0510 (8)
O221	0.8193 (3)	0.7837 (2)	0.05955 (16)	0.0786 (10)
O222	0.9951 (4)	0.8361 (3)	−0.0117 (2)	0.1098 (15)
O241	1.3842 (3)	0.5354 (3)	−0.1158 (2)	0.1143 (14)
O242	1.4466 (4)	0.3639 (3)	−0.0449 (2)	0.1165 (16)
O261	1.1055 (3)	0.4201 (3)	0.28120 (18)	0.0859 (11)
O262	1.1452 (4)	0.2773 (3)	0.2042 (2)	0.1313 (18)
N7	0.8110 (3)	0.6902 (2)	0.40887 (14)	0.0360 (8)
N22	0.9452 (3)	0.7616 (3)	0.03091 (18)	0.0576 (11)
N24	1.3682 (4)	0.4645 (4)	−0.0558 (2)	0.0789 (14)
N26	1.1265 (3)	0.3811 (3)	0.2124 (2)	0.0704 (14)
N50	0.5743 (3)	0.7204 (2)	0.58737 (15)	0.0420 (9)
C2	0.3433 (4)	0.6496 (3)	0.2533 (2)	0.0512 (14)
C3	0.4078 (4)	0.6092 (3)	0.3401 (2)	0.0478 (12)
C5	0.6373 (4)	0.5560 (3)	0.4149 (2)	0.0468 (14)
C6	0.7960 (4)	0.5690 (3)	0.4109 (2)	0.0469 (12)
C7	0.7792 (4)	0.7338 (3)	0.4931 (2)	0.0434 (11)
C8	0.9643 (4)	0.6940 (3)	0.3817 (2)	0.0459 (11)
C9	0.9829 (4)	0.8160 (3)	0.3542 (2)	0.0478 (12)
C10	0.1593 (4)	0.8149 (3)	0.5739 (2)	0.0505 (12)
C11	0.9013 (5)	0.9839 (3)	0.2563 (2)	0.0518 (14)
C12	0.8346 (4)	1.0285 (3)	0.1711 (2)	0.0539 (14)
C14	0.6076 (5)	1.0701 (4)	0.0954 (2)	0.0576 (14)
C15	0.4461 (5)	1.0692 (3)	0.1052 (3)	0.0575 (14)
C17	0.2817 (4)	0.9446 (3)	0.1365 (2)	0.0541 (14)
C18	0.2749 (4)	0.8188 (3)	0.1526 (2)	0.0538 (14)
C20	0.1216 (5)	0.7557 (3)	0.6477 (2)	0.0613 (16)
C21	1.0182 (3)	0.5728 (3)	0.12696 (19)	0.0404 (11)
C22	1.0425 (3)	0.6446 (3)	0.04981 (19)	0.0409 (10)
C23	1.1556 (4)	0.6113 (3)	−0.0077 (2)	0.0487 (11)
C24	1.2521 (3)	0.5014 (3)	0.0058 (2)	0.0496 (12)
C25	1.2404 (3)	0.4257 (3)	0.0777 (2)	0.0508 (12)
C26	1.1312 (3)	0.4619 (3)	0.13591 (19)	0.0431 (11)
C30	0.2334 (5)	0.6938 (3)	0.7049 (2)	0.0608 (14)
C40	0.3822 (4)	0.6879 (3)	0.6861 (2)	0.0506 (13)
C40*A*	0.4220 (4)	0.7432 (3)	0.60818 (19)	0.0414 (11)
C60	0.6144 (3)	0.7705 (3)	0.51535 (19)	0.0361 (10)
C60*A*	0.5108 (3)	0.8579 (2)	0.45982 (18)	0.0346 (10)
C70	0.5597 (3)	0.9253 (3)	0.39107 (18)	0.0409 (11)
C80	0.4585 (4)	1.0117 (3)	0.34246 (18)	0.0432 (11)
C90	0.3049 (4)	1.0333 (3)	0.3603 (2)	0.0473 (11)
C100	0.2551 (4)	0.9673 (3)	0.42736 (19)	0.0439 (11)
C10*A*0	0.3556 (3)	0.8794 (2)	0.47895 (18)	0.0336 (10)
C10*B*0	0.3102 (3)	0.8130 (3)	0.55319 (19)	0.0397 (11)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

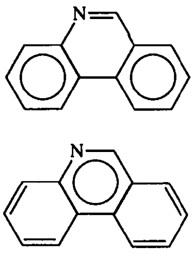
$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Na†	1/2	1/2	0.12155 (12)	0.0173 (11)
O1	0.2852 (6)	0.5673 (4)	0.0829 (2)	0.0207 (17)
O4	0.3440 (6)	0.3687 (4)	0.08539 (18)	0.0180 (17)
N7	0.5668 (6)	0.2900 (5)	0.1320 (2)	0.0157 (19)
N50	0.4307 (6)	0.3928 (4)	0.1975 (2)	0.0110 (17)
C2	0.1935 (7)	0.4956 (11)	0.0676 (2)	0.0183 (19)
C3	0.2648 (8)	0.4065 (6)	0.0490 (3)	0.019 (2)
C5	0.3898 (8)	0.2717 (7)	0.0747 (3)	0.018 (2)
C6	0.4547 (8)	0.2317 (6)	0.1180 (3)	0.016 (2)
C7	0.5965 (7)	0.2733 (6)	0.1818 (3)	0.0140 (19)
C8	0.6799 (8)	0.2641 (7)	0.1023 (3)	0.019 (2)
C9	0.7766 (8)	0.3454 (7)	0.1002 (3)	0.020 (2)
C10	0.2643 (7)	0.4868 (8)	0.3047 (3)	0.015 (2)
C20	0.1715 (9)	0.5452 (6)	0.2840 (3)	0.022 (3)
C30	0.1655 (8)	0.5533 (6)	0.2349 (3)	0.020 (3)
C40	0.2533 (7)	0.5024 (10)	0.2076 (2)	0.0167 (17)
C40*A*	0.3474 (8)	0.4420 (6)	0.2277 (3)	0.013 (2)
C60	0.5109 (11)	0.3287 (5)	0.2145 (2)	0.0097 (19)
C60*A*	0.5260 (6)	0.3096 (6)	0.2652 (3)	0.012 (2)
C70	0.6161 (7)	0.2414 (6)	0.2826 (3)	0.018 (2)
C80	0.6327 (7)	0.2304 (7)	0.3301 (3)	0.018 (2)
C90	0.5604 (8)	0.2890 (7)	0.3612 (3)	0.020 (3)
C100	0.4730 (8)	0.3550 (6)	0.3449 (3)	0.019 (3)
C10*A*0	0.4511 (7)	0.3664 (6)	0.2963 (3)	0.013 (2)
C10*B*0	0.3534 (8)	0.4339 (6)	0.2775 (3)	0.014 (2)
Cl	0.6861 (5)	0.0003 (5)	0.05224 (17)	0.124 (2)
C55†	0.7740 (18)	0	0	0.057 (6)
I†	0	0.22492 (6)	0	0.0266 (2)

† Atoms in special positions.



Kekulé's structures



Clar's structures

Scheme II. Kekulé's and Clar's canonical formulae.

dine can be described with five Kekulé's and two Clar's structures (Scheme II), which indicates domination of benzene structures and the C=N double bond at sites 5 and 6.

Bond lengths and angles observed in the structures studied and also in *[N,N′*-bis(6-phenanthridinyl-κ*N*-methyl)-7,16-diaza-18-crown-6-κ^4*O,O′,O″,O‴*] 1,2-dichloromethane potassium picrate (Alihodžić *et al.*, 1993) are in agreement with the proposed resonant formulae. Bond lengths in the (lateral) benzene rings are in the ranges 1.351 (7)–1.416 (6) Å in (1), 1.369 (5)–1.416 (4) Å in (2) and 1.355 (12)–1.426 (12) Å in (3) (Table 5). The largest deviation is 0.044 (7) Å from the benzene bond length 1.394 (7) Å (average

Table 5. *Selected bond lengths (Å) for (1)–(3)*

	(1)	(2)	(3)
Phenanthridine unit			
C10—C20	1.370 (8)	1.369 (5)	1.380 (12)
C20—C30	1.391 (8)	1.393 (5)	1.406 (12)
C30—C40	1.351 (7)	1.377 (6)	1.384 (12)
C40—C40*A*	1.416 (6)	1.407 (5)	1.397 (13)
C40*A*—N50	1.422 (5)	1.395 (5)	1.391 (10)
N50—C60	1.322 (5)	1.307 (4)	1.295 (11)
C60—C60*A*	1.410 (5)	1.448 (4)	1.477 (10)
C60*A*—C70	1.415 (6)	1.400 (4)	1.404 (11)
C70—C80	1.357 (7)	1.374 (5)	1.374 (12)
C80—C90	1.389 (7)	1.397 (5)	1.406 (12)
C90—C100	1.374 (7)	1.376 (5)	1.355 (12)
C60*A*—C10*A*0	1.412 (5)	1.416 (4)	1.407 (11)
C100—C10*A*0	1.394 (6)	1.404 (4)	1.413 (12)
C10—C10*B*0	1.409 (6)	1.411 (5)	1.405 (12)
C40*A*—C10*B*0	1.409 (6)	1.400 (5)	1.426 (12)
C10*A*0—C10*B*0	1.440 (6)	1.443 (4)	1.467 (11)
N50—C51	1.501 (6)		
C60—C61	1.490 (5)		
C7—C60		1.512 (5)	1.491 (12)
N7—C7		1.477 (4)	1.471 (10)
Macrocyclic ring			
O1—C2		1.421 (4)	1.426 (13)
O1—C9^{i}			1.426 (11)
C2—C3		1.490 (5)	1.505 (15)
C3—O4		1.425 (4)	1.421 (10)
O4—C5		1.419 (4)	1.420 (11)
C5—C6		1.502 (5)	1.508 (12)
C6—N7		1.465 (4)	1.464 (10)
N7—C8		1.470 (5)	1.495 (10)
C8—C9		1.503 (5)	1.488 (13)
C9—O10		1.425 (4)	
O10—C11		1.425 (4)	
C11—C12		1.481 (5)	
C12—O13		1.426 (5)	
O13—C14		1.411 (4)	
C14—C15		1.490 (7)	
C15—O16		1.431 (4)	
O16—C17		1.422 (4)	
C17—C18		1.492 (5)	
O1—C18		1.426 (4)	

	(1)	(2)	(3)
Coordination sphere around *M* (K for 2, Na for 3)			
M—O1		2.896 (2)	2.659 (6)
M—O4		2.822 (2)	2.613 (6)
M—O10		2.877 (2)	
M—O13		3.005 (2)	
M—O16		2.943 (2)	
M—N50			2.700 (6)
M—O		2.786 (3)	
M—O221		2.878 (3)	
Triflate anion			
S—C	1.796 (5)		
C—F1	1.327 (5)		
C—F2	1.326 (5)		
C—F3	1.339 (5)		
S—O2	1.432 (3)		
S—O3	1.430 (4)		
S—O5	1.426 (3)		
Dichloromethane			
Cl—C55			1.751 (11)
Picrate anion			
O—C21		1.240 (4)	
C21—C22		1.446 (4)	
C22—C23		1.373 (5)	
C23—C24		1.376 (5)	
C24—C25		1.380 (5)	
C25—C26		1.364 (4)	
C21—C26		1.451 (5)	
N22—C22		1.451 (5)	
N24—C24		1.443 (5)	
N26—C26		1.457 (4)	
O221—N22		1.208 (4)	
O222—N22		1.216 (5)	
O241—N24		1.220 (5)	
O242—N24		1.223 (6)	
O261—N26		1.221 (4)	
O262—N26		1.214 (5)	

Symmetry code: (i) $1 - x, 1 - y, z$.

value from neutron diffraction studies with $R \leq 0.08$: Bacon, Curry & Wilson, 1964; Boucherle, Gillon, Maruani & Schweizer, 1987; Stevens *et al.*, 1989). Deviations of 0–3° from the bond angle 120° are also found, thus confirming the geometry close to that typical of the benzene ring. It would be logical to expect changes in bond lengths involving the N atom bonded covalently or coordinatively. In phenanthridine (Brett, Rademacher & Boese, 1993) C—N bond lengths are 1.296 (3) and 1.397 (3) Å and the C—N—C bond angle is 117.8 (2)°. In (2) the phenanthridine N atom is not in the first coordination (Dietrich, Viout & Lehn, 1993) of the alkali atom, whereas in (3) the N atoms from both phenanthridine arms are coordinated to sodium. However, differences in bond lengths and angles of phenanthridine with respect to various chemical environments are within the limits of experimental errors (Table 5). The planarity of phenanthridine units was tested by calculating the best least-squares plane for the aromatic system. The phenanthridine unit in (1) is planar [the largest deviation is for C80, 0.019 (8) Å]. In (2) and (3) the phenanthridine units are not planar. The largest deviations reveal C40 [0.224 (7) Å] in (2) and C70 and C100 [0.11 (2) Å] in (3). The dihedral angles between lateral and central rings of the phenanthridine unit in (2) are 7.8 (2) and 7.2 (1)°.

3.2. *Cation binding in (2) and (3)*

In (2) a macrocyclic aza-18-crown-6 unit coordinates potassium with five O atoms (O1, O4, O10, O13 and O16) and two O atoms from picrate (phenol O and *ortho*-nitro group O221; Fig. 2). Chemically different ligands are positioned in such a way that the molecule is of C_1 symmetry. The values of K—O range from 2.786 (3) (phenol oxygen) to 3.005 (2) Å (Table 5). These values are longer than the sum of the ionic radii

Table 6. *Selected bond angles (°) for (1)–(3)*

	(1)	(2)	(3)
Phenanthridine unit			
C10—C20—C30	120.1 (4)	119.9 (4)	120.1 (8)
C20—C30—C40	120.5 (5)	120.4 (3)	119.5 (8)
C30—C40—C40*A*	120.9 (4)	119.9 (3)	121.5 (6)
C40—C40A—C10*B*0	119.2 (4)	120.0 (3)	118.9 (7)
C40*A*—C10*B*0—C10	118.0 (4)	118.0 (3)	118.9 (8)
C10*B*0—C10—C20	121.3 (4)	121.4 (3)	121.1 (8)
C40*A*—N50—C60	121.7 (3)	118.6 (3)	119.2 (6)
N50—C60—C60*A*	121.3 (3)	123.3 (3)	123.4 (7)
C60—C60*A*—C10*A*0	120.1 (3)	118.3 (2)	117.6 (7)
C60*A*—C10*A*0—C10*B*0	118.4 (4)	117.8 (2)	119.4 (7)
C10*A*0—C10*B*0—C40*A*	119.3 (3)	118.3 (3)	116.2 (7)
C10*B*0—C40*A*—N50	119.1 (4)	122.6 (3)	123.6 (7)
C60*A*—C70—C80	120.7 (4)	120.6 (3)	120.2 (8)
C70—C80—C90	120.1 (5)	120.6 (3)	119.6 (8)
C80—C90—C100	120.5 (4)	119.4 (3)	120.8 (8)
C90—C100—C10*A*0	121.0 (4)	121.4 (3)	121.1 (8)
C100—C10*A*0—C60*A*	118.4 (4)	118.6 (3)	118.0 (7)
C10*A*0—C60*A*—C70	119.3 (4)	119.4 (2)	120.2 (8)
C40*A*—N50—C51	118.8 (4)		
N50—C60—C61	119.6 (3)		
N50—C60—C7		115.8 (3)	119.0 (6)
C60—C7—N7		114.7 (3)	113.7 (6)
C7—N7—C6		111.4 (2)	110.5 (6)
Coordination sphere around *M* (K for 2, Na for 3)			
O—*M*—O1		130.21 (7)	
O—*M*—O4		91.54 (7)	
O—*M*—O10		78.95 (7)	
O—*M*—O13		116.06 (7)	
O—*M*—O16		134.35 (6)	
O—*M*—O221		56.76 (7)	
O1—*M*—O1^{i}			131.0 (2)
O1—*M*O4		58.75 (6)	62.5 (2)
O1—*M*O4^{i}			97.7 (2)
O1—*M*—O10		148.17 (6)	
O1—*M*—O13		107.82 (7)	
O1—*M*—O16		58.16 (6)	
O1—*M*—O221		121.90 (6)	
O4—*M*—O4^{i}			133.5 (2)
O4—*M*—O10		116.41 (6)	
O4—*M*—O13		147.27 (6)	
O4—*M*—O16		116.71 (6)	
O4—*M*—O221		140.48 (7)	
O10—*M*—O13		57.49 (7)	
O10—*M*—O16		113.70 (6)	
O10—*M*—O221		82.78 (7)	
O13—*M*—O16		56.28 (7)	
O13—*M*—O221		72.23 (6)	
O16—*M*—O221		80.57 (7)	
O1—*M*—N50			106.7 (2)
O1—*M*—N50^{i}			112.2 (2)
O4—*M*—N50			77.9 (2)
O4—*M*—N50^{i}			147.5 (2)
N50—*M*—N50^{i}			73.3 (2)
Macrocyclic ring			
O1—C2—C3		108.9 (3)	108.1 (6)
C2—C3—O4		108.8 (3)	108.3 (6)
C3—O4—C5		112.1 (2)	111.5 (6)
O4—C5—C6		109.3 (3)	107.6 (7)
C5—C6—N7		114.9 (3)	113.2 (7)
C6—N7—C8		108.8 (3)	110.7 (6)
N7—C8—C9		114.0 (3)	112.9 (7)
C9^{i}—O1—C2			110.8 (7)
C8—C9—O1^{i}			107.9 (7)
C8—C9—O10		110.1 (3)	
C9—O10—C11		110.8 (2)	
O10—C11—C12		110.7 (3)	
C11—C12—O13		108.8 (3)	
C12—O13—C14		112.1 (3)	
O13—C14—C15		108.6 (3)	
C14—C15—O16		109.3 (3)	
C15—O16—C17		111.5 (3)	
O16—C17—C18		109.2 (3)	
C17—C18—O1		108.8 (3)	
C18—O1—C2		112.7 (2)	
Picrate ligand			
O—C21—C22		125.8 (3)	
O—C21—C26		123.5 (3)	
C22—C21—C26		110.7 (3)	
C21—C22—C23		124.5 (3)	
C22—C23—C24		119.4 (3)	
C23—C24—C25		121.1 (3)	
C24—C25—C26		118.8 (3)	
C21—C26—C25		125.4 (3)	
N22—C22—C21		119.4 (3)	
N22—C22—C23		116.1 (3)	
N24—C24—C23		119.7 (3)	
N24—C24—C25		119.2 (3)	
N27—C26—C21		117.7 (3)	
N26—C26—C25		117.0 (3)	
O221—N22—O222		121.7 (3)	
O221—N22—C22		119.8 (3)	
O222—N22—C22		118.5 (3)	
O241—N24—O242		123.2 (3)	
O241—N24—C24		118.5 (3)	
O242—N24—C24		118.3 (3)	
O261—N26—O262		123.2 (3)	
O261—N26—C26		119.0 (3)	
O262—N26—C26		117.8 (3)	

Symmetry code: (i) $1 - x, 1 - y, z$.

[2.67 (Goldsmith, 1926) and 3.00 Å, for coordination 7 (Shannon, 1976)]. The average diameter of an 18-crown-6 cavity of 2.63 Å is smaller than the sum of the ionic radii. The shift of K^+ for 0.796 (8) Å out of the centre of cavity towards the picrate ligand is observed; the best least-squares plane of O1, O4, O10 and O13 was used as a reference plane. A macrocyclic O atom, O16, is displaced [0.589 (8) Å] in the same direction as K^+. The N7 atom can be treated as a second coordination (Dietrich, Viout & Lehn, 1993) [$K^+\cdots$N7 is 3.252 (2) Å].

The complex cation of (3) exhibits a crystallographic twofold axis. The macrocycle 7,16-diaza-18-crown-6 accommodates six-coordinated Na^+ [$Na^+\cdots$O1 2.659 (6) and $Na^+\cdots$O4 2.613 (6) Å (including their symmetry equivalents)], and N50 and N50^{i} atoms from phenanthridine units [$Na^+\cdots$N50 2.700 (6) Å]. The N7 and N7^{i} atoms are considered as the second coordination [$Na^+\cdots$N7 2.918 (7) Å]. The average diameter of the macrocyclic cavity is 2.09 Å. Although the diameter of Na^+ does not exceed the size of the cavity, the metal ion

Table 7. *Selected torsion angles (°) for (1)–(3)*

	(1)	(2)	(3)
Phenanthridine unit			
N50—C40*A*—C10*B*0—C10	179.3 (4)	169.8 (3)	−179.9 (10)
C10*A*0—C10*B*0—C40*A*—C40	−179.4 (4)	172.7 (3)	177.7 (8)
C100—C10*A*0—C60*A*—C60	180.0 (9)	177.5 (3)	−174.5 (7)
C10*B*0—C10*A*0—C60*A*—C70	179.1 (4)	−176.5 (3)	−177.2 (7)
C60*A*—C60—N50—C51	−179.9 (4)		
C61—C60—N50—C40*A*	179.4 (4)		
C40*A*—N50—C60—C7		−174.8 (3)	177.7 (7)
N7—C7—C60—N50		125.5 (3)	−7.5 (11)
C60—C7—N7—C8		161.5 (3)	159.7 (7)
C9—C8—N7—C7		−73.4 (3)	−81.5 (8)
Macrocyclic ring			
O1—C2—C3—O4		−64.6 (3)	58.5 (8)
C2—C3—O4—C5		−172.1 (3)	165.6 (7)
C3—O4—C5—C6		−174.4 (3)	−171.2 (6)
O4—C5—C6—N7		67.1 (3)	−63.1 (8)
C5—C6—N7—C8		−164.7 (3)	−78.9 (8)
C6—N7—C8—C9		164.3 (3)	155.9 (7)
N7—C8—C9—O10		−68.6 (3)	
N7—C8—C9—O1$^{\rm i}$			−57.3 (9)
C8—C9—O1$^{\rm i}$—C2$^{\rm i}$			−163.7 (6)
C8—C9—O10—C11		171.2 (3)	
C9—O10—C11—C12		173.6 (3)	
C9—O1$^{\rm i}$—C2$^{\rm i}$—C3$^{\rm i}$			178.9 (6)
O10—C11—C12—O13		64.4 (4)	
C11—C12—O13—C14		176.6 (3)	
C12—O13—C14—C15		−175.6 (3)	
O13—C14—C15—O16		−64.3 (4)	
C14—C15—O16—C17		175.7 (3)	
C15—O16—C17—C18		−179.5 (3)	
O16—C17—C18—O1		67.0 (3)	
C17—C18—O1—C2		177.1 (3)	
C18—O1—C2—C3		−173.0 (3)	

Symmetry code: (i) $1 - x, 1 - y, z$.

is shifted 1.067 (3) Å from the best least-squares plane (O1, O1$^{\rm i}$, O4 and O4$^{\rm i}$) towards the phenanthridine units. The *syn*-positioned antiparallel phenanthridine units are separated by 3.46 (1) Å, which is slightly larger than the sum of van der Waals radii (3.40 Å, Fig. 3). The solvent molecule dichloromethane is not coordinated to sodium. The cation charge is compensated by I$^-$.

3.3. *Picrate ligand in (2)*

The geometry of the picrate ion agrees quite well with that described by Nardelli *et al.* (1987), where the *para*-nitro group is found to be almost coplanar with the ring. Significant differences from benzene geometry are due to the considerable contribution of quinoid structures in the resonance forms of the picrate ion: C—O with high double-bond character and adjacent C—C bonds are longer [1.446 (4) and 1.451 (5) Å], whereas the two further C—C bonds are shorter [1.373 (5) and 1.364 (4) Å]. The largest deviations of intercyclic bond angles are at vertices C21 [110.7 (3)°], C22 [124.5 (3)°] and C26 [125.4 (3)°] (for numbering see Fig. 2). However, the mean value of the C—C—C angles is 120°. Both *ortho*-nitro groups are twisted from the plane of the aromatic ring with torsion angles O222—N22—C22—C23 −26.5 (4) and O262—N26—C26—C25 −42.0 (4)°. These values are in agreement with the analyses of Walkinshaw (1986) and De Ridder & Schenk (1995). In contrast, a *para*-nitro group is close to being planar with the aromatic ring [O241—N24—C24—C23 5.0 (5)°]. The mean value of the torsion angles of the aromatic ring is 2.1 (5)°.

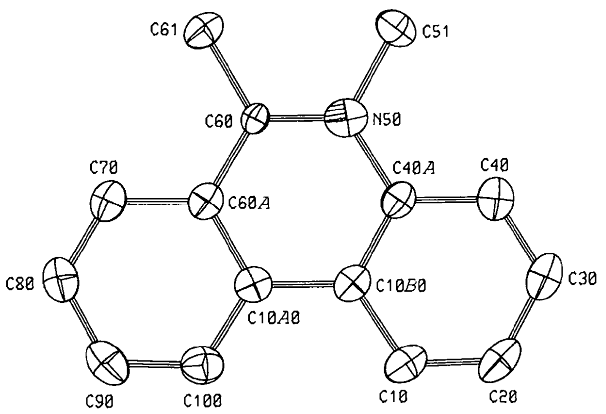


Fig. 1. *ORTEP*II (Johnson, 1976) diagram at the 30% probability level of the phenanthridinium unit of (1).

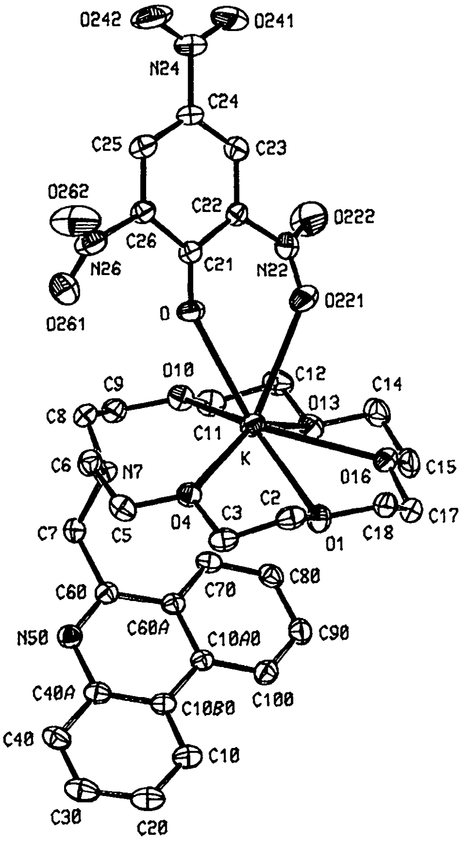


Fig. 2. *ORTEP*II (Johnson, 1976) drawing at the 30% probability level of the phenanthridinium unit of (2); the aza-18-crown-6 macrocycle with a single-armed phenanthridine unit and the picrato-$\kappa^2 O,O'$ ligand complexing potassium *via* seven O atoms.

3.4. *Conformations of macrocyclic rings in (2) and (3)*

The conformations of macrocyclic rings in (2) and (3) are shown in polar diagrams, see Fig. 4 (Dunsworth & Weiler, 1987). The conformational analysis of the macrocyclic polyether 18-crown-6 presented by Dobler (1984) recognized a crown-type conformation with an approximate D_{3d} symmetry to be highly populated (68%). Wipff, Weiner & Kollman (1982) have found that the macrocyclic ring conformation depends on the dielectric constant. With a low dielectric constant the lowest-energy structure is the same type (C_i) as also found in some crystal structures of 18-crown-6. In the more polar environment these authors calculated a D_{3d} structure of similar energy. They also predicted the presence of a C_1 structure which is comparable in energy to the lowest-energy centrosymmetric C_i and D_{3d} structures. The real symmetry of the aza-18-crown-6 macrocyclic ring of (2) is C_1 (Fig. 4*a*) as predicted by Wipff, Weiner & Kollman (1982). However, the approximate higher symmetry can be considered depending on the deviations which can be tolerated. Deviations between the values of torsion angles related by a hypothetic mirror plane are ~ 3.8° (Table 7). Thus, at first approximation it would be a C_s symmetry. However, losing the criteria, a pseudo-twofold axis (for two bond pairs the torsion angles are of opposite sign, *i.e.* t^- and t^+) might be accepted, resulting in an approximate C_{2h} symmetry. The exact C_{2h} symmetry imposed by crystallographic symmetry elements was observed in the macrocyclic 18-crown-6 with $Cu(NH_3)_4.H_2O.PF_6$ (Colquhoun, Stoddart & Williams, 1981).

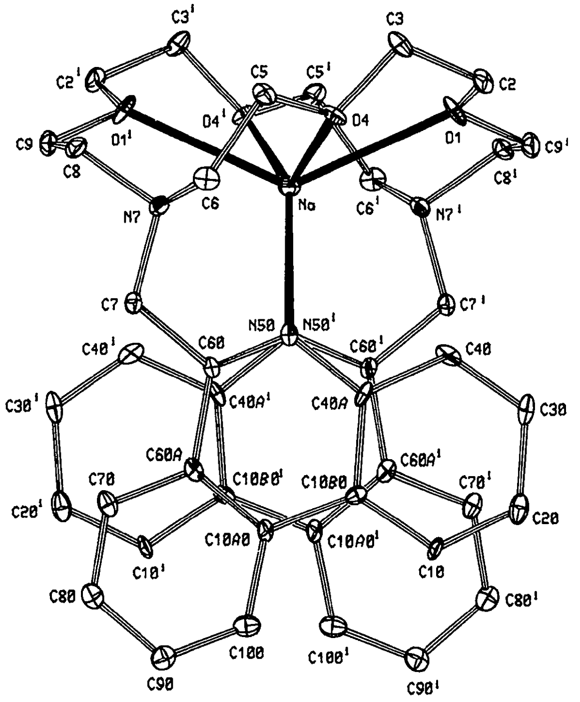


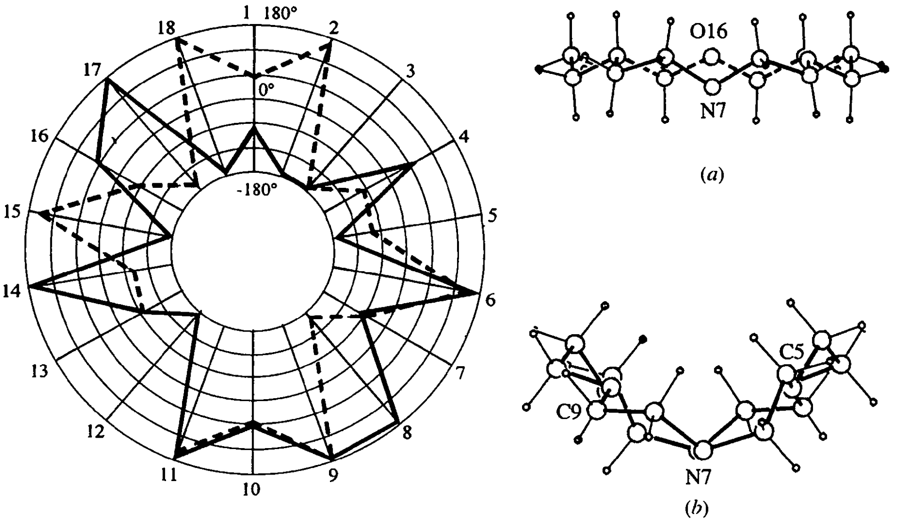
Fig. 3. *ORTEP*II (Johnson, 1976) drawing at the 30% probability level of (3); 7,16-diaza-18-crown-6 with two-armed phenanthridine antiparallel units including six-coordinated sodium shows a crystallographic twofold axis.

The conformation of 7,16-diaza-18-crown-6 in (3) is not crown type; it exhibits a crystallographic C_2 symmetry (Fig. 4*b*).

3.5. *Crystal packing of (1), (2) and (3)*

Packing diagrams are illustrated in Figs. 5–7.

In the crystal structure of (1) phenanthridinium cations *via* their methyl groups (C51 and C61) participate in the weak interactions of C—H···O type with triflate anions [C51—H511···O5($1+x$, y, $1+z$) 2.381 (6), C51—H512···O3(x, y, $1+z$) 2.519 (6), C61—H611···O3($x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 2.328 (6) and C61—H612···O2($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+$ z) 2.486 (6) Å].



(*a*)

(*b*)

Fig. 4. Polar diagram of the macrocyclic rings in (2) (heavy line) and (3) (dashed line); side views: (*a*) of (2) and (*b*) of (3).

A triflate anion is in the *gauche* conformation. The crystal packing of (2) is realized *via* van der Waals interactions only. In the crystal structure of (3) the complex cation exhibits a twofold symmetry with sodium located at a twofold axis ($\frac{1}{2}$, $\frac{1}{2}$, z). The iodine anion and dichloromethane are situated in the holes between the cations.

4. Evaluation of C—C and C—N bond lengths of phenanthridine by semi-empirical and molecular mechanics methods

The values of the C—C and C—N bond lengths of phenanthridine, obtained by X-ray structure determination (Brett, Rademacher & Boese, 1993), are compared with the calculated values using semi-empirical methods and molecular mechanics (Table 8). The initial coordinates from X-ray structure were used for optimization by various procedures. For the semi-empirical approach *AM*1 and *PM*3 (package *MOPAC*, Version 6.00, incorporated into *DISCOVER*, Version 2.95) were used. Molecular mechanics results were obtained by various force fields: *MM*3 (1992) and *DISCOVER* 2.95-CFF91 (Biosym Technologies, 1994). Good agreement between experimental and calculated values for *AM*1

Table 8. *Bond lengths of phenanthridine (Å) (Brett, Rademacher & Boese, 1993) compared with values obtained by semi-empirical methods and molecular mechanics*

	X-ray data	*AM*1	*PM*3	*DISCOVER*	*MM*3
C10—C20	1.377 (3)	1.381	1.376	1.383	1.383
C20—C30	1.401 (3)	1.404	1.401	1.403	1.409
C30—C40	1.373 (3)	1.380	1.380	1.391	1.383
C40—C40*A*	1.406 (3)	1.422	1.412	1.368	1.414
C40*A*—N50	1.397 (3)	1.398	1.410	1.362	1.396
N50—C60	1.296 (3)	1.306	1.308	1.344	1.301
C60—C60*A*	1.432 (3)	1.450	1.445	1.384	1.443
C60*A*—C70	1.406 (3)	1.408	1.408	1.435	1.416
C70—C80	1.381 (3)	1.382	1.378	1.380	1.381
C80—C90	1.403 (3)	1.405	1.404	1.411	1.409
C90—C100	1.374 (3)	1.383	1.378	1.386	1.383
C100—C10*A*0	1.408 (3)	1.412	1.409	1.417	1.420
C60*A*—C10*A*0	1.415 (3)	1.415	1.405	1.426	1.407
C10*A*0—C10*B*0	1.447 (3)	1.446	1.446	1.403	1.458
C10—C10*B*0	1.411 (3)	1.407	1.411	1.424	1.420
C40*A*—C10*B*0	1.418 (3)	1.427	1.407	1.404	1.412

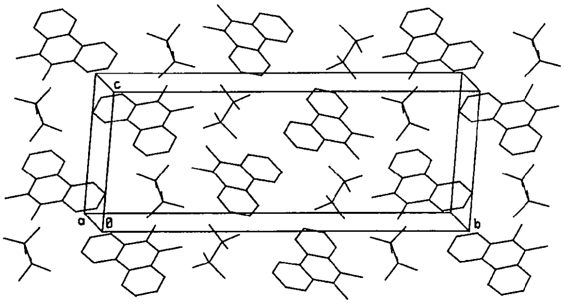


Fig. 5. Crystal packing of (1).

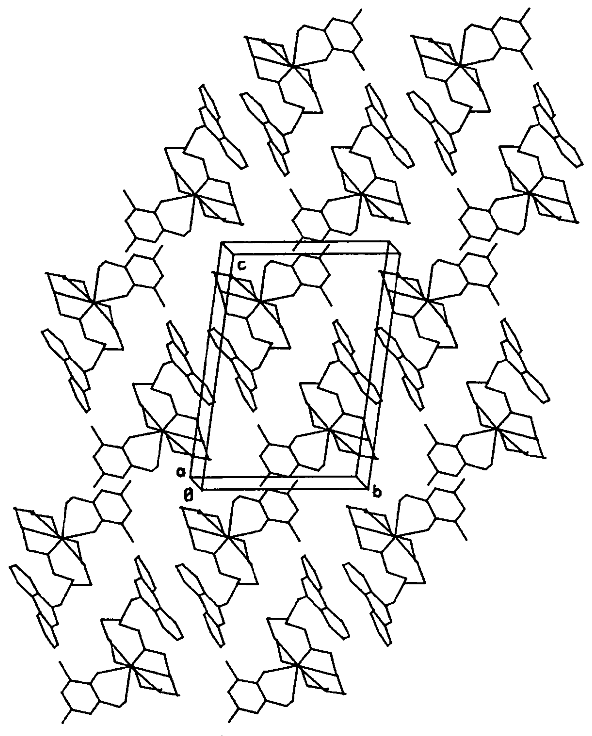


Fig. 6. Crystal packing of (2).

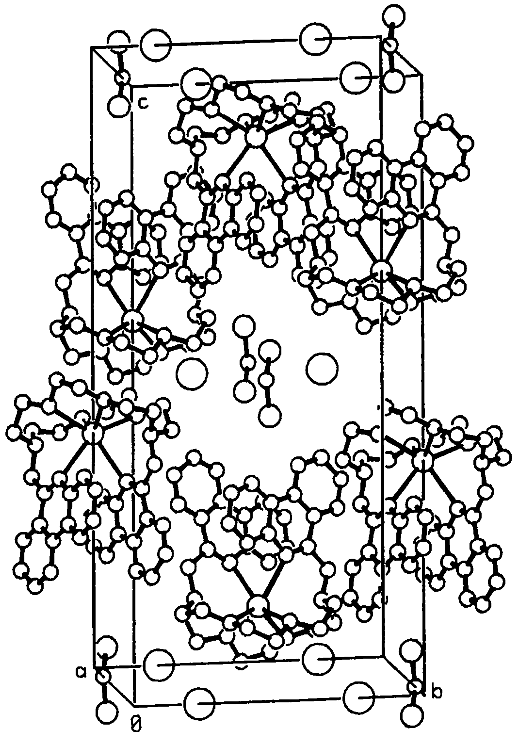


Fig. 7. Crystal packing of (3) with iodine and solvent molecules stacked between 7,16-diaza-18-crown-6 complex cations.

(maximum differences to the experimental values are 0.006 Å and 0.4°), *PM*3 (maximum differences 0.005 Å and 0.9°) and *MM*3 (maximum differences 0.007 Å and 0.4°) were obtained. However, differences based on the calculations from *DISCOVER* are significantly larger, *i.e.* 0.021 Å and 1.2°. This can be explained by parameterization in the CFF91 force field, which uses values of single, double and aromatic (benzene) bonds only. A phenanthridine system with a central aromatic ring includes one bond with Pauling's (1951) π-bond order of $\frac{4}{5}$ (N50—C60) and three with $\frac{1}{5}$ (C40*A*—N50, C60—C60*A* and C10*A*0—C10*B*0). Particularly, for these bonds and adjacent ones in lateral rings (C40—C40*A*, C60*A*—C70), the differences between experimental and calculated values (CFF91) are the largest. The theoretical aspects of the bond character will be discussed in the next section.

5. Valence bond and Hückel molecular orbital treatment of bond length–bond order relations for benzenoid hydrocarbons, azabenzenoid hydrocarbons and picrate-like systems

Most recent carbon–carbon bond length–Pauling bond order relations for benzenoid hydrocarbons are either linear (Herndon, 1974; Herndon & Párkányi, 1976) or non-linear (Pauling, 1980). In order to test the relations with a larger number of more accurate structure data a new search of the Cambridge Structural Database (1995, October Release) was performed. The search was extended for azabenzenoid hydrocarbons and picrate-like aromatic systems as well. The general conditions of the search were: structures solved either by X-ray or neutron diffraction with *R* less than 0.07; disordered structures and those with significant geometry deviations due to various errors were excluded. Benzenoid hydrocarbons and azabenzenoid hydrocarbons were extracted from the base with the additional requirements: a benzenoid system was not allowed to be substituted or be part of a π-complex or any type of metal complex or organometallic compound, but could occur as a solvate, clathrate or as a constitutive part of a molecular complex. The planar systems were chosen, with torsion angles of the neighbouring C and N atoms deviating from 0 or 180° a maximum of 5°. Whenever possible, the unsubstituted structures were taken.

Picrate-like systems were based on the 1,3,5-trinitrobenzenes substituted with hydroxy or oxy groups. The structure of 2-((picryloxy)methyl)pyridine was additionally extracted from the base as a structure with formal single and double C—C bonds.

The C—C bond lengths in all three classes of the molecules, C—N in azabenzenoids and C—O in picrate-like systems are averaged according to the molecular symmetry, molecules in the asymmetric unit and in some cases those obtained from the data reported by several different authors (for the same compound). This comprises 14 benzenoid hydrocarbons with 124 C—C bonds, which represents a greater database than previous works [*e.g.* nine molecules, 82 bonds (Pauling, 1980); 13 molecules, 92 bonds (Herndon & Párkányi, 1976)]; seven azabenzenoid hydrocarbons with 11 C—N and 77 C—C bonds; ten picrate-like systems (molecules and anions) with 27 C—C and ten C—O bonds (Table 9). The average values for a free picrate anion from the CSD search were taken. The structural formulae represented by a single Kekulé structure each, with bond labels, compound names and refcodes, are given in Scheme III.

Enumeration of unexcited Kekulé structures and determination of Pauling's π-bond orders were carried out using the method proposed by Randić (1975). The Coulson C—C π-bond orders in benzenoid hydrocarbons were taken from the literature (Streitwieser & Brauman, 1965) and also applied to the C—C bonds in azabenzenoid hydrocarbons; the Coulson bond orders were found for 110 C—C bonds from the benzenoid hydrocarbons and for all bonds from the azabenzenoid hydrocarbons. Experimental bond lengths with e.s.d.'s and Pauling's and Coulson's bond orders are given in Table 9.

Linear regression analyses were perfomed in the form $d = a - bp$, where d is a bond length in Å, a and b are regression coefficients and (p) is a Pauling (p_P) or Coulson (p_C) π-bond order. All regression analyses were carried out on unweighted data. The results of the analyses are listed in Table 10. The equation for C—N bonds is graphically presented in Fig. 8.

6. Conclusions

Regression analysis results based on Pauling's bond orders in benzenoid hydrocarbons are found to be comparable to those of Herndon & Párkányi [1976 (average e.s.d. 0.006 Å, Table 10)]. Both types of bond orders, Pauling's (VB) and Coulson's (HMO) bond orders, are similar for the C—C bonds in benzenoid hydrocarbons

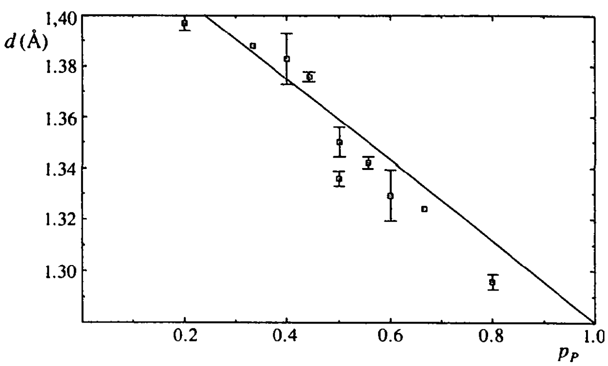
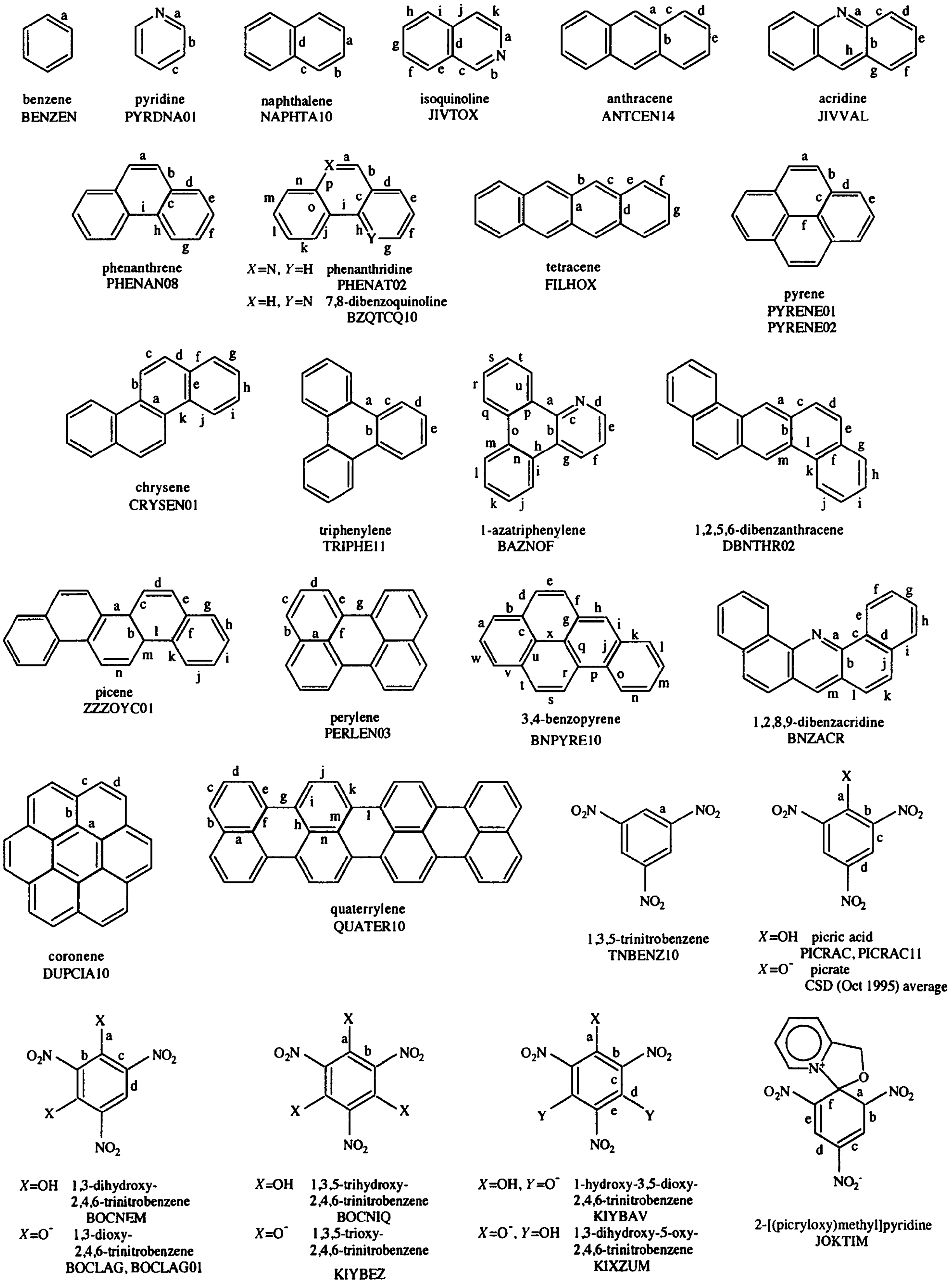


Fig. 8. Linear dependence of the aromatic carbon–nitrogen bond length on Pauling's bond order. The plot is based on 11 bonds, two of which are of the same value. For these two bonds and an additional one the literature does not report the standard deviations.



Scheme III. Chemical diagrams of compounds listed in Table 9.

Table 9. *Experimental bond lengths* (d), Pauling (p_P) and Coulson (p_C) π-bond orders used in regression analysis of bond length–bond order relationships*

Molecule	Bond	d (Å)	p_P	p_C
Benzenoid hydrocarbons				
Benzene	a	1.390 (9)	0.500	0.667
Naphthalene	a	1.407 (2)	0.333	0.603
	b	1.371 (2)	0.667	0.725
	c	1.422 (2)	0.333	0.555
	d	1.420 (2)	0.333	0.518
Anthracene	a	1.395 (3)	0.500	0.606
	b	1.432 (3)	0.250	0.485
	c	1.428 (3)	0.250	0.535
	d	1.353 (4)	0.750	0.737
	e	1.418 (5)	0.250	0.586
Phenanthrene	a	1.338 (5)	0.800	0.775
	b	1.422 (7)	0.200	0.506
	c	1.413 (7)	0.400	0.542
	d	1.414 (4)	0.400	0.575
	e	1.349 (8)	0.600	0.707
	f	1.381 (9)	0.400	0.623
	g	1.376 (4)	0.600	0.702
	h	1.391 (7)	0.400	0.590
	i	1.454 (6)	0.200	0.461
Tetracene	a	1.442 (2)	0.200	0.458
	b	1.405 (2)	0.400	0.584
	c	1.388 (2)	0.600	0.618
	d	1.441 (2)	0.200	0.475
	e	1.434 (2)	0.200	0.530
	f	1.349 (2)	0.800	0.741
	g	1.415 (2)	0.200	0.581
Triphenylene	a	1.469 (8)	0.111	0.428
	b	1.411 (9)	0.444	0.562
	c	1.405 (9)	0.444	0.603
	d	1.385 (10)	0.556	0.690
	e	1.390 (11)	0.444	0.637
Chrysene	a	1.402 (2)	0.500	0.573
	b	1.437 (2)	0.250	0.538
	c	1.331 (2)	0.750	0.754
	d	1.417 (2)	0.250	0.521
	e	1.417 (2)	0.375	0.535
	f	1.415 (2)	0.375	0.568
	g	1.361 (2)	0.625	0.712
	h	1.392 (2)	0.375	0.617
	i	1.370 (2)	0.625	0.707
	j	1.409 (2)	0.375	0.583
	k	1.453 (2)	0.250	0.476
Pyrene	a	1.347 (4)	0.833	0.777
	b	1.429 (4)	0.167	0.503
	c	1.417 (3)	0.333	0.524
	d	1.400 (4)	0.500	0.594
	e	1.380 (5)	0.500	0.669
	f	1.423 (3)	0.333	0.536
Perylene	a	1.426 (2)	0.333	0.526
	b	1.411 (2)	0.333	0.552
	c	1.359 (3)	0.667	0.707
	d	1.393 (2)	0.333	0.629
	e	1.384 (2)	0.667	0.644
	f	1.429 (2)	0.333	0.529
	g	1.471 (2)	0.000	0.414
1,2,5,6-Dibenzanthracene	a	1.391 (2)	0.500	0.605
	b	1.426 (2)	0.333	0.513
	c	1.438 (2)	0.167	0.501
	d	1.338 (2)	0.833	0.778
	e	1.436 (2)	0.167	0.499
	f	1.413 (2)	0.417	0.544
	g	1.412 (2)	0.417	0.579
	h	1.360 (2)	0.583	0.703
Azabenzenoids				
Pyridine	a	1.336 (3)	0.500	
	b	1.381 (3)	0.500	0.667
	c	1.377 (3)	0.500	0.667
Isoquinoline	a	1.388	0.333	
	b	1.324	0.667	
	c	1.410	0.333	0.555
	d	1.410	0.333	0.518
	e	1.416	0.333	0.555
	f	1.359	0.667	0.725
	g	1.411	0.333	0.603
	h	1.364	0.667	0.725
	i	1.418	0.333	0.555
	j	1.421	0.333	0.555
	k	1.343	0.667	0.725
Acridine	a	1.350	0.500	
	b	1.429	0.250	0.485
	c	1.425	0.250	0.535
	d	1.364	0.750	0.737
	e	1.399	0.250	0.586
	f	1.345	0.750	0.737
	g	1.436	0.250	0.535
	h	1.385	0.500	0.606
Phenanthridine	a	1.296 (3)	0.800	
	b	1.432 (3)	0.200	0.506
	c	1.415 (3)	0.400	0.542
	d	1.406 (3)	0.400	0.575
	e	1.381 (3)	0.600	0.707
	f	1.403 (3)	0.400	0.623
	g	1.374 (3)	0.600	0.702
	h	1.408 (3)	0.400	0.590
	i	1.447 (3)	0.200	0.461
	j	1.411 (3)	0.400	0.590
	k	1.377 (3)	0.600	0.702
	l	1.401 (3)	0.400	0.623
	m	1.373 (3)	0.600	0.707
	n	1.406 (3)	0.400	0.575
	o	1.418 (3)	0.400	0.542
	p	1.397 (3)	0.200	
7,8-Dibenzoquinoline	a	1.388 (10)	0.800	0.775
	b	1.375 (10)	0.200	0.506
	c	1.419 (10)	0.400	0.542
	d	1.441 (10)	0.400	0.575
	e	1.341 (10)	0.600	0.707
	f	1.391 (10)	0.400	0.623
	g	1.329 (10)	0.600	
	h	1.383 (10)	0.400	
	i	1.431 (10)	0.200	0.461
	j	1.350 (10)	0.400	0.590
	k	1.439 (10)	0.600	0.702
	l	1.389 (20)	0.400	0.623
	m	1.330 (10)	0.600	0.707
	n	1.409 (10)	0.400	0.575
	o	1.419 (10)	0.400	0.542
	p	1.420 (10)	0.200	0.506
1-Azatriphenylene	a	1.464 (2)	0.111	0.428
	b	1.404 (2)	0.444	0.562
	c	1.376 (2)	0.444	
	d	1.342 (2)	0.556	
	e	1.387 (2)	0.444	0.637
	f	1.368 (2)	0.556	0.690
	g	1.395 (2)	0.444	0.603
	h	1.459 (2)	0.111	0.428
	i	1.407 (2)	0.444	0.603

Table 9 (*cont.*)

Molecule	Bond	d (Å)	p_P	p_C
	i	1.403 (2)	0.417	0.626
	j	1.373 (2)	0.583	0.697
	k	1.406 (2)	0.417	0.595
	l	1.455 (2)	0.167	0.451
	m	1.397 (2)	0.500	0.629
Picene	a	1.429 (7)	0.308	0.493
	b	1.388 (9)	0.462	0.563
	c	1.412 (9)	0.231	0.532
	d	1.367 (8)	0.769	0.758
	e	1.410 (10)	0.231	0.517
	f	1.414 (9)	0.385	0.537
	g	1.414 (8)	0.385	0.570
	h	1.367 (9)	0.615	0.710
	i	1.366 (10)	0.385	0.619
	j	1.409 (9)	0.615	0.705
	k	1.394 (10)	0.385	0.586
	l	1.469 (8)	0.231	0.470
	m	1.430 (10)	0.308	0.554
	n	1.406 (8)	0.692	0.732
3,4-Benzopyrene	a	1.378 (13)	0.444	0.658
	b	1.401 (12)	0.556	0.604
	c	1.414 (12)	0.333	0.522
	d	1.434 (12)	0.111	0.493
	e	1.342 (13)	0.889	0.784
	f	1.447 (12)	0.111	0.493
	g	1.444 (11)	0.222	0.486
	h	1.361 (12)	0.667	0.641
	i	1.419 (12)	0.333	0.562
	j	1.410 (11)	0.333	0.517
	k	1.425 (12)	0.333	0.552
	l	1.374 (14)	0.667	0.721
	m	1.397 (14)	0.333	0.609
	n	1.364 (13)	0.667	0.710
	o	1.419 (12)	0.333	0.580
	p	1.435 (12)	0.333	0.489
	q	1.395 (11)	0.444	0.556
	r	1.423 (11)	0.222	0.539
	s	1.352 (12)	0.778	0.754
	t	1.441 (12)	0.222	0.520
	u	1.418 (11)	0.333	0.524
	v	1.412 (12)	0.444	0.580
	w	1.376 (14)	0.556	0.680
	x	1.419 (11)	0.333	0.538
Coronene	a	1.424	0.300	0.522
	b	1.420	0.400	0.538
	c	1.414	0.300	0.538
	d	1.372	0.700	0.745
Quaterrylene	a	1.420 (4)	0.333	
	b	1.417 (4)	0.333	
	c	1.367 (4)	0.667	
	d	1.401 (4)	0.333	
	e	1.382 (4)	0.667	
	f	1.431 (4)	0.333	
	g	1.468 (4)	0.000	
	h	1.431 (4)	0.333	
	i	1.383 (4)	0.667	
	j	1.383 (4)	0.333	
	k	1.389 (4)	0.667	
	l	1.462 (4)	0.000	
	m	1.429 (4)	0.333	
	n	1.431 (4)	0.333	
	j	1.372 (2)	0.556	0.690
	k	1.387 (2)	0.444	0.637
	l	1.377 (2)	0.556	0.690
	m	1.397 (2)	0.444	0.603
	n	1.408 (2)	0.444	0.562
	o	1.462 (2)	0.111	0.428
	p	1.405 (2)	0.444	0.562
	q	1.399 (2)	0.444	0.603
	r	1.373 (2)	0.556	0.690
	s	1.391 (2)	0.444	0.637
	t	1.362 (2)	0.556	0.690
	u	1.397 (2)	0.444	0.603
1,2,8,9-Dibenzacridine	a	1.350 (6)	0.500	
	b	1.419 (8)	0.333	0.513
	c	1.455 (6)	0.167	0.453
	d	1.427 (7)	0.333	0.544
	e	1.411 (13)	0.417	0.494
	f	1.399 (10)	0.583	0.698
	g	1.408 (9)	0.417	0.626
	h	1.377 (11)	0.583	0.703
	i	1.434 (9)	0.417	0.579
	j	1.419 (11)	0.167	0.498
	k	1.367 (9)	0.833	0.780
	l	1.463 (9)	0.167	0.498
	m	1.388 (8)	0.500	0.611
Picrate-like species				
1,3,5-Trinitrobenzene	a	1.379 (7)	0.500	
Picric acid	a	1.335 (6)	0.000	
	b	1.403 (6)	0.500	
	c	1.376 (6)	0.500	
	d	1.374 (6)	0.500	
Picrate†	a	1.249	0.429	
	b	1.445	0.286	
	c	1.368	0.571	
	d	1.379	0.429	
1,3-Dihydroxy-2,4,6-trinitrobenzene	a	1.326 (4)	0.000	
	b	1.393 (4)	0.500	
	c	1.402 (4)	0.500	
	d	1.370 (4)	0.500	
1,3-Dioxy-2,4,6-trinitrobenzene	a	1.269 (11)	0.364	
	b	1.418 (10)	0.364	
	c	1.440 (13)	0.273	
	d	1.395 (10)	0.500	
1,3,5-Trihydroxy-2,4,6-trinitrobenzene	a	1.319 (3)	0.000	
	b	1.404 (3)	0.500	
1,3,5-Trioxy-2,4,6-trinitrobenzene	a	1.245 (9)	0.323	
	b	1.452 (8)	0.338	
1,3-Dihydroxy-5-oxy-2,4,6-trinitrobenzene	a	1.246 (6)	0.429	
	b	1.453 (4)	0.286	
	c	1.396 (5)	0.571	
	d	1.327 (5)	0.000	
	e	1.409 (4)	0.429	
1-Hydroxy-3,5-dioxy-2,4,6-trinitrobenzene	a	1.326 (7)	0.000	
	b	1.402 (11)	0.500	
	c	1.484 (10)	0.273	
	d	1.238 (11)	0.364	
	e	1.428 (13)	0.364	
2-[(Picryloxy)methyl] pyridine	a	1.500	0.000	
	b	1.367	0.667	
	c	1.373	0.333	
	d	1.385	0.333	
	e	1.358	0.667	
	f	1.493	0.000	

* E.s.d.'s were taken from original papers or calculated from those of atomic coordinates (for anthracene) wherever possible. † Averaged values for free picrate are taken from the Cambridge Structural Database search (October 1995 release).

Table 10. *Regression analysis results for benzenoid hydrocarbons, azabenzenoids and picrate-like systems*

Bond type	Bond order*	a†	b†	r†	δ (Å)‡	σ (Å)§	s (Å)¶	Class of molecules
C—C	p_P	1.464 (3)	0.143 (6)	0.898	0.010	0.006	0.014	Benzenoid hydrocarbons
	p_C	1.591 (7)	0.315 (12)	0.928	0.008	0.006	0.011	
C—C	p_P	1.462 (6)	0.143 (13)	0.783	0.013	0.006	0.019	Azabenzenoids
	p_C	1.571 (14)	0.283 (23)	0.820	0.011	0.006	0.017	
C—N	p_P	1.444 (10)	0.184 (18)	0.959	0.006	0.005	0.009	
C—C	p_P	1.497 (11)	0.212 (25)	0.862	0.015	0.007	0.021	Picrate-like systems
C—O	p_P	1.326 (5)	0.198 (18)	0.968	0.007	0.008	0.011	

* Pauling's (p_P) and Coulson's (p_C) π-bond orders. † Regression coefficients (a) and (b) of a regression equation $d = a - bp$, where (p) is π-bond order and (r) is the corresponding correlation coefficient. ‡ Average deviation (δ) calculated from experimental bond lengths. § Average e.s.d.'s (σ) of experimental bond lengths. ¶ Standard error of estimate (s).

Table 11. *Experimental and calculated bond lengths (Å) of the phenanthridine aromatic system*

	Phenanthridine*	(1)	(2)	(3)	VB theory†	VB theory‡	MO theory§	MO theory¶
C60—N50	1.296 (3)	1.322 (5)	1.307 (4)	1.295 (11)	1.297	1.297	-	-
C40*A*—N50	1.397 (3)	1.422 (5)	1.395 (5)	1.391 (10)	1.407	1.407	-	-
C60*A*—C60	1.432 (3)	1.410 (5)	1.448 (4)	1.477 (10)	1.435	1.433	1.432	1.428
C40*A*—C10*B*0	1.418 (3)	1.409 (6)	1.400 (5)	1.426 (12)	1.409	1.407	1.420	1.418
C60*A*—C10*A*0	1.415 (3)	1.412 (5)	1.416 (4)	1.407 (11)				
C40—C40*A*	1.406 (3)	1.416 (6)	1.407 (5)	1.397 (13)	1.407	1.405	1.410	1.408
C60*A*—C70	1.406 (3)	1.415 (6)	1.400 (4)	1.404 (11)				
C30—C40	1.373 (3)	1.351 (7)	1.377 (6)	1.384 (12)	1.378	1.376	1.368	1.371
C70—C80	1.381 (3)	1.357 (7)	1.374 (5)	1.374 (12)				
C20—C30	1.401 (3)	1.391 (8)	1.393 (5)	1.406 (12)	1.407	1.405	1.395	1.395
C80—C90	1.403 (3)	1.389 (7)	1.397 (5)	1.406 (12)				
C10—C20	1.377 (3)	1.370 (8)	1.369 (5)	1.380 (12)	1.378	1.376	1.370	1.372
C90—C100	1.374 (3)	1.374 (7)	1.376 (5)	1.355 (12)				
C10—C10*B*0	1.411 (3)	1.409 (6)	1.411 (5)	1.405 (12)	1.407	1.405	1.405	1.404
C100—C10*A*0	1.408 (3)	1.394 (6)	1.404 (4)	1.413 (12)				
C10*A*0—C10*B*0	1.447 (3)	1.440 (6)	1.443 (4)	1.467 (11)	1.435	1.433	1.446	1.441

* Experimental bond lengths of phenanthridine (Brett, Rademacher & Boese, 1993). † Calculated bond lengths using the equation $d = 1.444 - 0.184\,p_P$ for C—N bonds and $d = 1.464 - 0.143\,p_P$ for C—C bonds, where (p_P) are Pauling's π-bond orders. ‡ Calculated bond lengths using the equation $d = 1.444 - 0.184\,p_P$ for C—N bonds and $d = 1.462 - 0.143\,p_P$ for C—C bonds, where (p_P) are Pauling π-bond orders. § Calculated bond lengths using the equation $d = 1.591 - 0.315\,p_C$ for C—C bonds, where (p_C) are Coulson's π-bond orders. ¶ Calculated bond lengths using the equation $d = 1.572 - 0.283\,p_C$ for C—C bonds, where (p_C) are Coulson's π-bond orders.

and azabenzenoid hydrocarbons. The average difference in C—C bonds in azahydrocarbons and chemically analogous C—C bonds in benzenoid hydrocarbons is 0.013 Å. Differences between the regression coefficients for the C—C bonds in benzenoid hydrocarbons and azabenzenoids calculated by the Pauling and Coulson methods are within the limits of two standard deviations (Table 10). The aromatic C—N bonds linearly depend on the Pauling bond orders (Fig. 8).

The comparison of the experimental values of the C—N and C—C bonds in (1), (2), (3) and phenanthridine (Brett, Rademacher & Boese, 1993) with those evaluated by Pauling's and Coulson's type of bond length–bond order calculations (Tables 9 and 10) can be summarized as follows (Table 11).

(*a*) Compound (1) with the 5,6-dimethylphenanthridinium cation reveals the largest deviations of all bond lengths, particularly in the central ring, from the theoretical values.

(*b*) Good agreement was observed between the experimental bond lengths of unsubstituted phenathridine and calculated values.

(*c*) The C—N bond lengths in (2), (3) and phenanthridine agree well with the calculated values. The influence of the phenanthridine coordination to a metal atom in (3) (first coordination) on the C—N bonds was not observed.

(*d*) The largest deviations of the experimental values of C60—C60*A* (Figs. 2 and 3) from the calculated ones were observed in (2) and (3) (0.020 and 0.049 Å, respectively) and C10*A*0—C10*B*0 in (3) (0.034 Å), whereas other C—C bonds show deviations not larger than those detected in experimental values. The values obtained for bond lengths by Pauling's and Coulson's methods do not reveal significant differences ($\langle \Delta \text{C—C} \rangle = 0.004$ Å).

The present analysis based on the large number of data reveals both methods to be applicable for the aromatic systems such as benzenoid and azabenzenoid hydrocarbons. The optimized geometry of phenanthridine obtained by semi-empirical methods (*AM*1 and *PM*3) and molecular mechanics (*MM*3) reproduces well the approaches of Pauling and Coulson.

In order to see if the coordination of picrate to a metal (compound 2) can influence the geometry of the ligand itself the bond lengths in the picrate of (2) were compared with those of free picrate molecules (Cambridge Structural Database, 1995, October Release) and picric acid (Duesler, Englemann, Curtin & Paul, 1978; Srikrishnan, Soriano-Garcia & Parthasarathy, 1980). The analysis does not show differences larger than the experimental errors of the selected bonds. Therefore, the experimental values of bond lengths in (2) can be compared with the calculated ones. The bond length–bond order relations reproduce most of the bond lengths correctly; the only deviations were observed for the bonds C23—C24 and C24—C25 (average deviation 0.028 Å).

This work was supported by the Ministry of Science and Technology, Republic of Croatia.

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