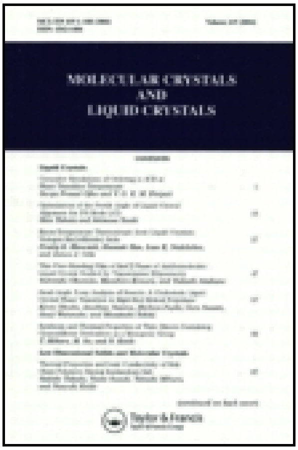


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Azoalkane-DDQ Arrays in the Solid State. New Donor-Acceptor Interactions for Crystal Engineering

M. L. Greer [a] & Silas C. Blackstock [a]

[a] Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama, 35487-0336

To cite this article: M. L. Greer & Silas C. Blackstock (1998): Azoalkane-DDQ Arrays in the Solid State. New Donor-Acceptor Interactions for Crystal Engineering, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 55-64

To link to this article: http://dx.doi.org/10.1080/10587259808044259

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 55–64
Reprints available directly from the publisher
Photocopying permitted by license only

Azoalkane-DDQ Arrays in the Solid State. New Donor-Acceptor Interactions for Crystal Engineering

M. L. Greer and Silas C. Blackstock*
Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336

A new set of donor-acceptor (DA) complexes between azoalkanes and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) is reported. Bis(cis-azoalkane)s are found to bind DDQ in solution, with complex formation constants in CH_2Cl_2 that range from 22 - 76 M^{-1}. Bis(azo)/DDQ crystalline solids are isolable and their crystal structures have been determined. Short intermolecular contacts in the crystals between the azo nitrogens and quinone ring carbons of 2.9 - 3.1 Å denote D--A "bonds" whose geometry is consistent with azo HOMO (n*) / DDQ LUMO (π*) overlap. The DA "bonding" promotes one-dimensional supramolecular ordering in the cocrystal which is organized as parallel $(\text{-DD-A-})_n$ strands. Thus, the azo/DDQ DA "bond" serves as a new crystal engineering synthon for preparing one-dimensional, two-component solids.

Keywords: crystal engineering; donor-acceptor complexes; azoalkanes; DDQ

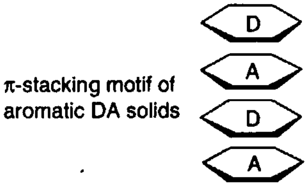
INTRODUCTION

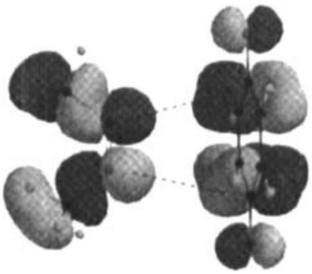
The construction of solid-state molecular architectures to yield materials with designed mechanical, optical, or electronic properties is a significant goal of contemporary chemical research.[1] In the field of crystal engineering,[2] this goal applies to the domain of the molecular crystal and is accomplished using specific functional group interactions which combine to achieve some degree of intermolecular order in the lattice. Specific noncovalent associations between unlike functionality (hetereofunctional interactions) may provide a degree of chemoselectivity for controlling single and multi-component crystallization.

Our work has focused on the development of new organic donor-acceptor (DA) interactions[3] as synthons for the preparation of ordered solid phases.[4] Numerous examples of π-stacked DA cocrystals containing (mostly aromatic) extended π systems are known[3d] in which the general packing motif is one of parallel, alternating D and A rings separated by 3.3 - 3.4 Å (plane-to-plane) to form columns (see below). Control of intermolecular torsion angles within a column is generally not possible in this motif, perhaps because the molecular separation is too great.

DA interactions between smaller, more localized organic functional groups are not as numerous in the literature and their crystal packing influences are not as well known. Our own studies have focused on 2-3 atom donor functions whose DA interactions we expect to yield especially short and hopefully topologically specific DA "bonds."

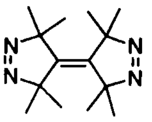
By matching donor HOMO and acceptor LUMO topologies for optimal orbital overlap, we have targeted various functional groups for analysis. Cis-azoalkanes are weak n* donors[5] whose HOMO appears well matched for overlap with the quinone π* LUMO, so we hypothesized that n*/π* association between these functions might occur. Furthermore, if bis(azo) donors (DD) are employed, then one-dimensionally ordered $(\text{-DD-A})_n$ cocrystalline solids might form. This turns out to be the case, as reported here for three bis(azoalkane) donors with the quinone acceptor 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ).



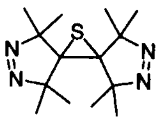


RESULTS

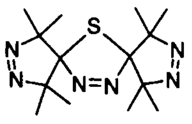
Our study employs bis(azoalkane)s **1** - **3** (shown below) as donors for interaction with DDQ. These bis(pyrazoline) substrates are known from the work of Bushby and coworkers.[6]



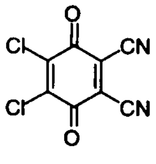
1



2



3



DDQ

Solution mixtures of DDQ and these weak donors are red, showing long-wavelength absorptions that are not observed for solutions of the individual components. The new absorptions are assigned as DA complex charge-transfer (CT) transitions and occur at λ_m of 464, 470, and 476 nm, respectively for DDQ mixtures with donors **1**, **2**, and **3** in CH_2Cl_2 as shown in Figures 1 - 3.

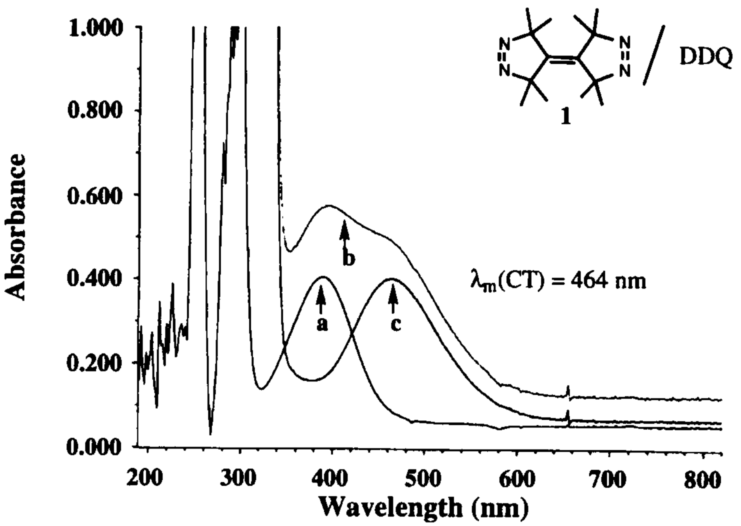


FIGURE 1 UV-vis spectra in CH_2Cl_2 of (a) 0.396 mM DDQ; (b) 0.396 mM DDQ and 22.3 mM **1**; and (c) spectrum b - spectrum a.

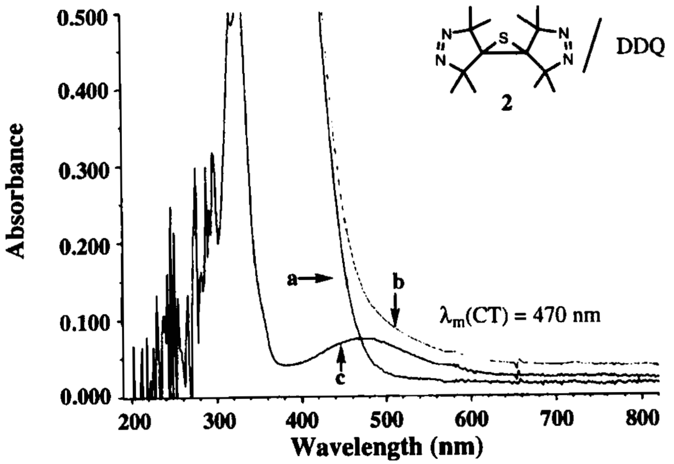


FIGURE 2. UV-vis spectra in CH_2Cl_2 of (a) 1.01 mM DDQ; (b) 1.01 mM DDQ and 2.32 mM **2**; and (c) spectrum b - spectrum a.

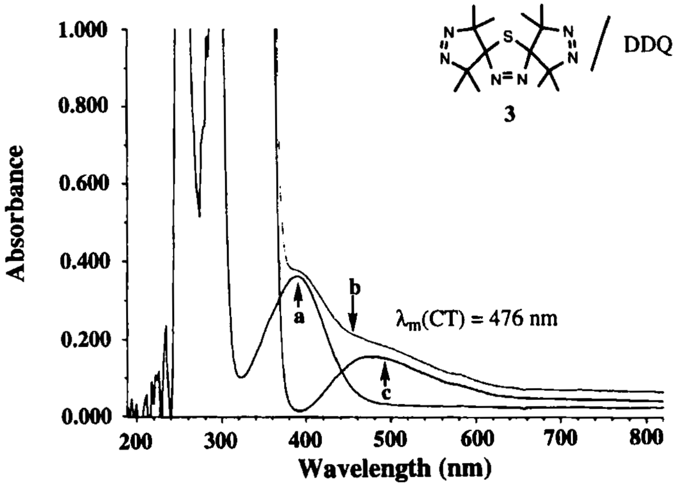


FIGURE 3. UV-vis spectra in CH_2Cl_2 of (a) 0.396 mM DDQ; (b) 0.396 mM DDQ and 18.4 mM **3**; and (c) spectrum b - spectrum a.

Benesi-Hildebrand analysis[7] of the DA mixtures yields K_f values for complex formation of 20.5±1.3, 76.2±1.5, and 50.0±17.4 M^{-1} in CH_2Cl_2, for **1**:DDQ, **2**:DDQ, and **3**:DDQ, respectively.[8]

Complex Crystal Structures

Cooled solutions of 1:1 DDQ:**1** produce dichroic red/yellow DA crystals of (**1**)DDQ whose crystal structure is depicted in Figures 4 and 5. Close D--A contacts of 2.92 and 3.00 Å between the azo nitrogens and the DDQ carbonyl carbons are observed.[9] The DDQ molecule is disordered in this crystal such that it is half unique and the chloro- and cyano- groups each have 50% site occupancy. For clarity, only one DDQ orientation is shown in the Figures. The geometry of DA complex has the azo plane at about 70° to the DDQ plane with the azo N=N bond axis parallel to the C=O bond axes in DDQ. The D-A links in (**1**)DDQ yield one-dimensional $(\text{-DD-A-})_n$ infinite chains as the primary structure of the lattice. Adjacent chains run parallel to each other with a staggering of adjacent interchain DD and A groups (Figure 5).

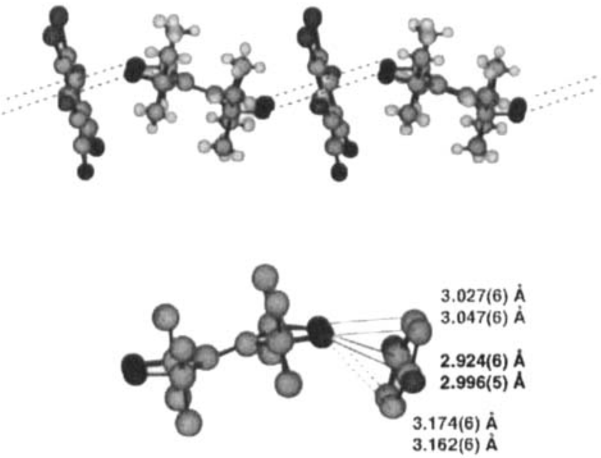


FIGURE 4. The $(\text{-DD-A-})_n$ chain in crystal (**1**)DDQ (above) and a blow-up of the D--A geometry (below).

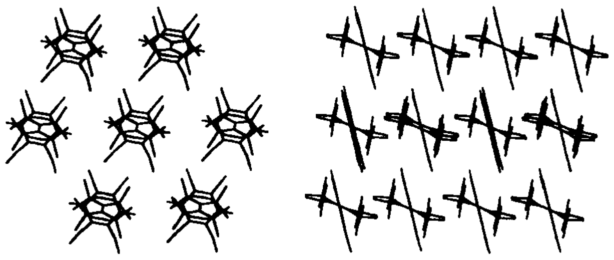


FIGURE 5. Crystal packing diagram for (1)DDQ: end view of hexagonally packed (-DD-A-)$_n$ chains (left) and side view (right).

Complex crystals of (2)DDQ are obtained from 1:1 mixtures in CH_2Cl_2. The X-ray structure of these dichroic yellow/red crystals is summarized in Figures 6 and 7. As for (1)DDQ, the lattice is composed of parallel (-DD-A-)$_n$ chains. The D--A topology again reflects apparent n*/ π* overlap between components. Interestingly, the DDQ molecule is not disordered in (2)DDQ and the chain stereochemistry has aligned DDQs and aligned thiiranes within a strand. The D and A dipoles orient in roughly opposite directions off the strand axis.

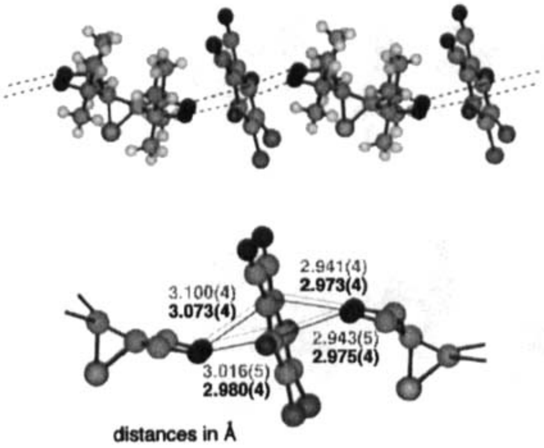


FIGURE 6. The (-DD-A-)$_n$ chain in crystal (2)DDQ (above) and a blow-up of the D--A--D triad geometry (below).

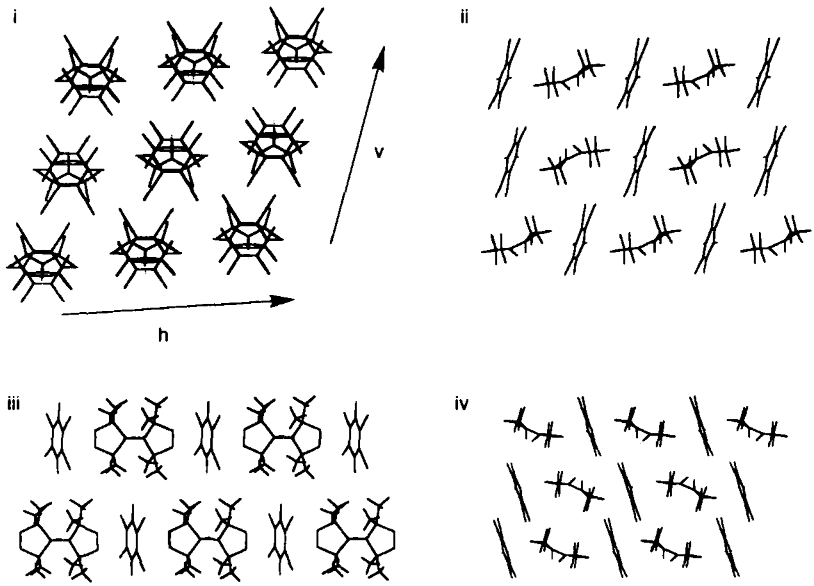
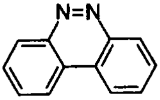


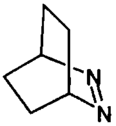
FIGURE 7. Crystal packing diagrams of (**2**)DDQ (i) axial view of strand packing, (ii) lateral view of vertical strand packing, (iii) lateral view of horizontal strand packing, and (iv) lateral view of diagonal strand packing.

DISCUSSION

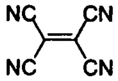
The above structures are the first reported azoalkane / DDQ complexes. The azo-DDQ-azo triad topology observed is chemically analogous to that previously found in D-A-D aggregates within crystalline benzo[c]cinnoline (**4**) / DDQ[10] and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) / tetracyanoethylene (TCNE)[5] crystals. In all these cases, the D-A "bonding" appears to be influenced by FMO donor n* / acceptor π^* interactions. The AM1-calculated n* HOMO-1 for donor **1** and the AM1-calculated π^* LUMO for DDQ are shown below. For **1**, the HOMO is predicted to be the (inaccessible) olefin π orbital, with the more chemically significant HOMO-1 azo n* orbital being 0.1 eV lower in energy. Likewise for TI(bp)$_2$, the AM1 calculated HOMO is the (sterically shielded) thiirane n-orbital on sulfur, with the azo n* combination orbitals being HOMO-1 and HOMO-2.



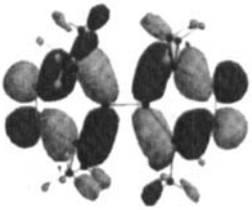
4



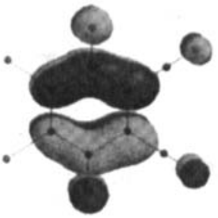
DBO



TCNE



donor **1** HOMO-1 by AM1



DDQ LUMO by AM1

A key supramolecular feature of the bis(azo) / DDQ structures from a crystal engineering standpoint is their one-dimensional character which is mediated by mutually bridging DD and A component interactions. The DDQ disorder observed in the (-**1**-DDQ-)$_n$ strand is not surprising since there is are no obvious secondary structural features present within (or between) strands to distinguish the cyano and chloro sites in the azo-DDQ-azo triad topology. On the other hand, it is noteworthy that the dipolar thiirane donor **2** yields DDQ-ordered and thiirane-ordered (-**2**-DDQ-)$_n$ chains, presumably due to dipolar interactions between the D and A components within (and perhaps also between) strands. The AM1-derived dipole moments of **2** and DDQ are 2.00 and 2.94 debyes, respectively.

CONCLUSION

These results show that azolkanes form robust complexes with DDQ in solution and in the solid state. The azo-DDQ interaction is sufficient to command one-dimensional ordering (i.e. strand formation) in crystals of linear bis(azo) donors **1** and **2** with DDQ. The dipolar nature of donor **2** and acceptor DDQ appears to facilitate their mutual ordering within the strands via dipolar interactions between adjacent strand components.

EXPERIMENTAL

Bis(pyrazolines) **1** - **3** were synthesized as previously reported[6] and DDQ (Aldrich) was recrystallized from $CHCl_3$. Crystal X-ray diffraction was performed on a Siemens SMART diffractometer with CCD area detection at 173 K using monochromatic MoK_α radiation, $\lambda = 0.71073$ Å. Solution and refinement (against $|F^2|$) were performed using SHELXTL. No absorption correction was employed. Hydrogen atoms were placed in calculated positions (0.95 Å from the methyl carbons with tetrahedral angles) and given torsional freedom while their thermal parameters were set to 1.2 x Ueq of the bonded carbon atom. Detailed structural results have been deposited to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK).

(1)DDQ. Bis(azo) **1** (35.7 mg, 0.14 mmol) and DDQ (31.1 mg, 0.14 mmol) were dissolved in 20 mL CH_2Cl_2/CH_3CN (1:1). Slow evaporation of the solvent at 25 °C yielded red/yellow dichroic crystals. mp 220-225 °C dec; IR (KBr, cm^{-1}) 1698 (s), 1567 (s), 1171 (s), 792 (s), 701 (s); UV-vis (CH_2Cl_2) λ_m 464 nm, (solid as Nujol mull) λ_m 470 nm. Crystal dimensions: 0.12 x 0.20 x 0.22 mm; triclinic P-1; a = 8.2158(4), b = 8.4423(4), c = 9.5845(4) Å, $\alpha = 76.063(2)°$, $\beta = 65.166(2)°$, $\gamma = 70.583(2)$, V = 565.19(5) $Å^3$, $d_{calc} = 1.397$ g/cm^3; $2.36 \leq \theta \leq 22.49°$; 1205 unique data, 221 parameters; R = 0.0677, $wR_2 = 0.1787$, GOF = 1.190.

(2)DDQ. Bis(azo) **2** (29.8 mg, 0.11 mmol) and DDQ (26.7 mg, 0.12 mmol) were dissolved in 10 mL CH_2Cl_2. Slow evaporation of the solvent at 25 °C yielded red/yellow dichroic crystals. mp 198-201 °C dec; IR (KBr, cm^{-1}) 1698 (s), 1567 (s), 1171 (s), 793 (s), 709 (s); UV-vis (CH_2Cl_2) λ_m 470 nm, (solid as Nujol mull) λ_m 490 nm. Anal. Calcd for $C_{22}H_{24}SCl_2N_6O_2$: C, 52.07; H, 4.77; N, 16.56. Found: C, 52.07; H, 4.69; N, 16.49. Crystal dimensions: 0.20 x 0.30 x 0.30 mm; triclinic P-1; a = 9.6092(4), b = 9.6652(4), c = 13.6693(6) Å, $\alpha = 77.154(2)°$, $\beta = 85.820(2)°$, $\gamma = 71.448(2)$ V =1173.44(9) $Å^3$, $d_{calc} = 1.436$ g/cm^3; $1.53 \leq \theta \leq 27.80°$; 5239 unique data (4770 [$I>2\sigma(I)$]), 395 parameters; R = 0.0617, $wR_2 = 0.1399$, GOF = 0.985.

(3)DDQ. Tris(azo) **3** (10.3 mg, 0.03 mmol) and DDQ (8.1 mg, 0.04 mmol) were dissolved in 1.25 mL CH_3CN. Cooling of the solution at -20 °C yielded deep reddish-purple crystals. mp 203-205 °C dec; IR (KBr, cm^{-1}) 1696 (s), 1588 (s), 1174 (s), 793 (s), 712 (s); UV-vis (CH_2Cl_2) λ_m 476 nm, (solid as Nujol mull) λ_m 510 nm. Anal. Calcd for $C_{22}H_{24}SCl_2N_8O_2$: C, 49.35; H, 4.52; N, 20.93. Found: C, 49.45; H, 4.52; N, 21.02.

Acknowledgments

The authors thank R. D. Rogers and L. Rogers for assistance with the X-ray crystal structures and the NSF and the donors to the petroleum research fund administered by the ACS for funding.

References

[1.] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*; (VCH, New York, 1995), b) F. Vogtle, *Supramolecular Chemistry: An Introduction* (John Wiley and Sons, New York, 1991).

[2.] For reviews of crystal engineering see a) G. R. Desiraju, *Crystal engineering: The Design of Organic Solids* (Elsevier, Amsterdam, 1989), b) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **28**, 37 (1995).

[3.] For reviews of DA chemistry see a) H. A. Bent, *Chem. Rev.*, **68**, 587 (1968), b) R. S. Mulliken, W. B. Person, *Molecular Complexes: A Lecture and Reprint Volume*; (Wiley-Interscience, New York, 1969), c) R. Foster, *Organic Charge-Transfer Complexes* (Academic Press, New York, 1969), Chap. 8, d) F. H. Herbstein, *Persp. Struct. Chem.*, **4**, 166, (1971).

[4.] a) S. C. Blackstock, K. Poehling, M. L. Greer, *J. Am. Chem. Soc.*, **117**, 6617, (1995), b) M. L. Greer, S. C. Blackstock, *J. Org. Chem.*, **61**, 7895, (1996), c) M. L. Greer, B. J. McGee, R. D. Rogers, S. C. Blackstock, *Angewandte Chemie* (1997), in press; d) M. L. Greer, J. R. Duncan, J. L. Duff, S. C. Blackstock, *Tetrahedron Lett.* (1997), in press.

[5.] S. C. Blackstock, J. K. Kochi, *J. Am. Chem. Soc.*, **109**, 2484, (1987).

[6.] a) R. J. Bushby, M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 2401, (1979), b) R. J. Crawford, H. Tokunaga, *Can. J. Chem.*, **52**, 4033, (1974), c) H. Quast, A. Fuss, H. Jakobi, *Chem. Ber.*, **124**, 1747, (1991).

[7.] H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703, (1949).

[8.] 1:1 complexation is assumed for the analysis, although deviations from this stoichiometry may occur, in which case the K_f values should be considered effective values. see D. A. Deranleau, *J. Am. Chem. Soc.*, **91**, 4050, (1969).

[9.] Van der Waal N--C contact is 3.25 Å. see A. J. Bondi, *J. Phys. Chem.*, **68**, 441, (1964).

[10.] B. Shaanan, U. Shmueli, M. Colapietro, *Acta Cryst.*, **B38**, 818 (1982)