

Supplementary information for *CrystEngComm* Paper

## Trimorphism of Model Carcinogen 4-Nitroquinoline-N-oxide<sup>†</sup>

Yakov P. Nizhnik, Jian Jiang Lu, Sergiy V. Rosokha and Jay K. Kochi,  
Department of Chemistry, University of Houston,  
Houston TX 77204 USA  
Fax: 713-743-2709; Tel: 713-743-3293;  
E-mail: srosokha@uh.edu

### Synthesis of 4-nitroquinoline N-oxide<sup>1,2</sup>

74 ml of 30 % hydrogen peroxide was added to a solution of 97 ml (106,1 g; 0.822 mol) of freshly distilled (*in vacuo*) quinoline in 245 ml of 99.7% acetic acid, and the mixture was heated and stirred at 65-70°C for 3 hours. Then, 66 ml of hydrogen peroxide was added, and the mixture was stirred at 65-70°C for 6 hours. The reaction mixture was concentrated in vacuum, and the residue was basified by the cautious addition of saturated solution of Na<sub>2</sub>CO<sub>3</sub> with stirring. The reddish-brown solution was extracted with chloroform (4×200 ml). The extract was dried over MgSO<sub>4</sub> overnight, filtered and brown oil containing quinoline N-oxide was obtained after chloroform evaporation under reduced pressure. 205 ml of 95-98 % sulfuric acid was cautiously added to this oil. 52 ml of 68-70% nitric acid was added portionwise over a period of 40 min with frequent stirring at 65-70°C, and the mixture was heated during 3 hours at 70°C. Then the mixture was cooled, put on ice and addition of 3 l of water resulted in precipitation of 4-nitro-quinoline-N-oxide as the yellow sediment. It was filtered on Buchner funnel, washed with water, 5% solution of Na<sub>2</sub>CO<sub>3</sub> to neutral reaction, water and small amount of ethanol. Residue was dried on air (137 g) and recrystallised from acetone as yellow needle crystals. Yield 103 g (66 % based on quinoline). M.p. 154°C (lit. data 153-154°C).

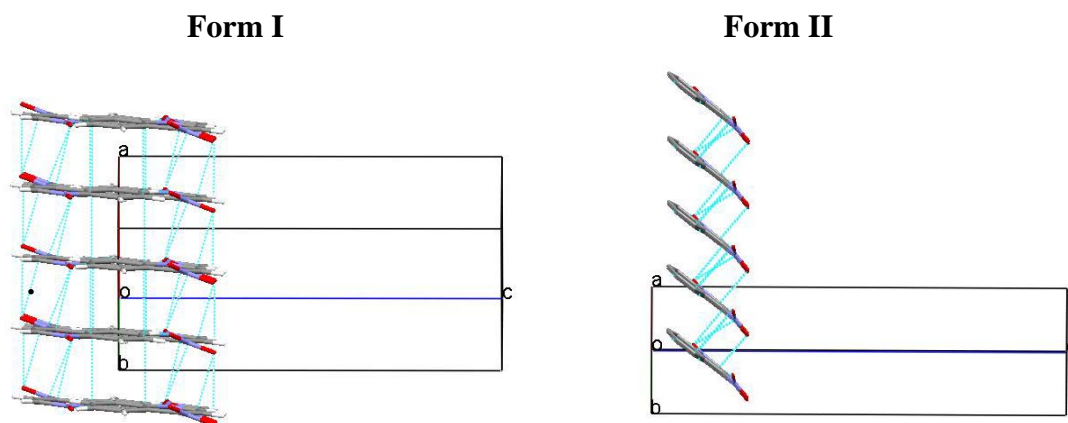
**Note:** **NQO** should be handled with care. Proper ventilation, protective gloves and safety glasses should be used. Nitrogroup can be easily replaced on chlorine in mixture of concentrated hydrochloric acid acetonitrile (1:10) at room temperature during the 1-2 days, yielding 4-chloroquinoline N-oxide,<sup>3,4</sup> so this system may be successfully used to utilize the residue of **NQO**.

1. E. Ochiai, *Aromatic Amine Oxides*; Elsevier: Amsterdam, London, New York. 1967.
2. E. Ochiai, *J. Org. Chem.*, 1953, **18**, 534.
3. V. P. Andreev, E. G. Kalistratova and A. V. Ryzhakov, *Chem. Heterocycl. Comp. (Latvia)*, 1996, **32**, 449.
4. V. P. Andreev and Y. P. Nizhnik, *Russ. J. Org. Chem.* 2001, **37**, 143.

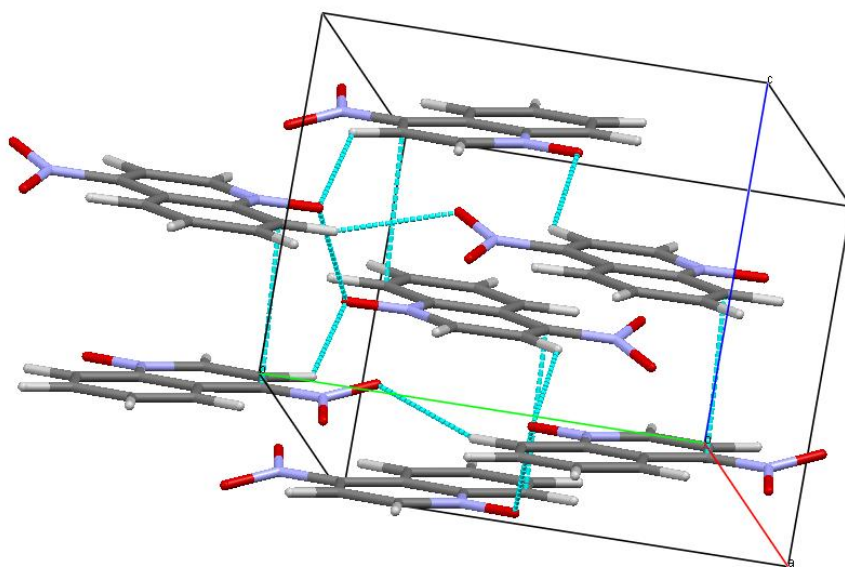
Table S1. IR-spectral characteristics of polymorphs of **NQO** (in  $\text{cm}^{-1}$ ).<sup>a</sup>

Form I	Form II	Form III	Assignment	Calculated frequencies <sup>b</sup>
<i>3126 w</i>	<i>3131 w</i>	<i>3117 w</i>	v(C-H)	3196(17)
<i>3099 w</i>	<i>3112 w</i>	<i>3097 w</i>		3180(8)
1588 w	1590 w	1590 w		1633(75) NO <sub>2</sub> (asymm) stretch + C-H bending
1565 m	1566 m	1565 m		1614(113) NO <sub>2</sub> (asymm) + ring stretch
<i>1518 s</i>	<i>1514 s</i>	<i>1514 s</i>	v <sub>as</sub> (NO <sub>2</sub> )	1575(103) NO <sub>2</sub> (asymm) stretch+ C-H bending
<i>1507.5 m</i>	<i>1507 w</i>	<i>1506 sh</i>		1560(49)
<i>1498 w</i>	<i>1496 w</i>			1482(30)
1445 w	1444 w	1446 w		1471(14)
1427 m-w	1425 w	1427 w		1429(91)
1388 m	1387 m	1387.5 m		1381(14)
<i>1356 w</i>	<i>1356 w</i>	<i>1355 w</i>	v <sub>s</sub> (NO <sub>2</sub> )	
<i>1342 m</i>	<i>1344 m</i>	<i>1339 m</i>		
<i>1333 m</i>	<i>1333 m</i>	<i>1330 m</i>		1374 (59) NO <sub>2</sub> (symm) + ring stretching
<i>1297 sh. vs</i>	<i>1299 vs</i>	<i>1299 vs</i>	v(N-O)	1339(609) NO <sub>2</sub> (symm) + NO stretching
<i>1293 vs</i>	<i>1289.5 vs</i>	<i>1289 sh</i>		1288(10)
1258 w	1257 w	1260 w		1283(2)
1237 m	1242 m	1242 w		1219(36)
1200 w	1199 w	1198 m		1196(5)
<i>1163 w</i>	<i>1166 m</i>	<i>1165 w</i>		1182(70)
<i>1156 m</i>	<i>1151 s</i>	<i>1155 s</i>		1156(16)
<i>1129 w</i>	<i>1130 m</i>	<i>1132 m</i>		1094(3)
1068 w	1066 w	1069 w		1057(20)
1030 w	1028 w	1030 w		1010(56)
1000 w	1001 w	998 sh		1008(4)
988 w	991	987 m		984(1)
967 w	964 w			965(4)
938 w	941 w	945 w		
926 w				
876 w	873 w	873 w		887(0.3)
<i>836 w</i>	<i>843 m</i>	<i>845 m</i>	δ(NO <sub>2</sub> )	854 (16) (NO <sub>2</sub> scissoring)
<i>829 s</i>	<i>835 w</i>	<i>834 m</i>	γ(CH)	841(31) (C-H wagging)
793 w	790 w	788 w-m		803(10)
769 w	773 m			
764 vs	767 s	766 vs		783(74) (C-H wagging)
736 s	739 s	739 s		756(12)
722 w	725 w	727 w		732 (5.5)

i) Bands in IR-spectra which were used for the identification of polymorphs of **NQO** are shown in italics. Note, that bands assignment was done based on the Gaussian 98 (B3LYP/6-311G\* Freq) calculations<sup>c</sup> together with the analysis of the related data in the next references: A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 1958, 2192. A. R. Katritzky and A. R. Hands, *J. Chem. Soc.*, 1958, 2195. H. Shindo, *Chem Pharm Bull.*, 1956, **6**, 117; P. Plaza, F. Le Guiner, M. Joyeux, N.Q. Dao, J. Zyss and R. Hierle, *J. Mol. Struct.*, 1991, **247**, 363; M. Joyeux, M. T. C. Martins Costa, D. Rinaldi and N. Q. Dao, *Spectrochimica Acta*, 1989, **45A**, 967; M. Joyeux and N. Q. Dao, *Spectrochimica Acta*, 1988, **44A**, 1447; E. Lorenz, M. Maczka, K. Hermanowicz, A. Waskowska, A. Puszko and J. Hanuza, *Vibrational Spectroscopy*, 2005, **37**, 195; J. Hanuza, J. Michalski, M. Maczka, Z. Talik and J. H. van der Maas, *Vibrational Spectroscopy*, 2002, **33**, 229. b) In parenthesis – calculated intensities, in KM/mole. c) Extensive hydrogen bonding in NQO crystals is apparently major reason of deviations between band positions measured for different polymorphs, as well as between experimental and calculated values.



**Fig.S1.** Layers of parallel NQO molecules in crystal lattices of forms I and II.



**Fig.S2.** Crystal lattice of form III of NQO ((R. S. Basalaev, T. A. Semenova and L. A. Aleshina, private communication) .