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Synthesis of Dipolar Nitronyl Nitroxides

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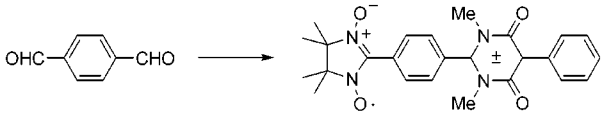
ABSTRACT



The synthesis of a nitronyl nitroxide radical with a dipolar (mesomeric betaine) unit is reported.

Since the discovery of nitronyl nitroxides (NIT) by Ullman et al.,[1] this class of radicals has attracted considerable interest as units for the preparation of molecular based magnets.[2] In 1991 ferromagnetic ordering in a NIT radical was observed.[3] Since then numerous publications have appeared that illustrate the use of NIT as building block(s) for magnetic materials.[4] One of the challenges in this field is the design of crystals with ferromagnetic ordering of the radical units.[5]

As a rational design of crystals with these properties is still lacking, it is interesting to study the effects of highly dipolar moieties upon the structure−property relationship of the compounds. In this paper we report the synthesis of a NIT radical with a pyrimidiniumolate unit[6] starting with terephthalaldehyde **1**. Acetalization with triethylorthoformiate[10] to the corresponding monoacetal (67%) with subsequent Willgerodt−Kindler reaction ($MeNH_2$, S) yields thioamide **2** (69%). Treatment of **2** with methyliodide and then with methylamine gives amidine **3** (83%, two steps).[12] Heating **3** with phenyl-bis(2,4,6-trichlorophenyl)-malonate[13] in anisole (reflux, 3 min) yields pyrimidiniumolate **4** (69%).

Removal of the protecting group (Lewatit S 100 furnishes the corresponding aldehyde (88%), which in treatment with 2,3-bis(hydroxylamino)-2,3-dimethylbutane yields **5** as nearly colorless crystals (52%). Dehydrogenation could be ac-

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(6) Mesomeric betaines[7] of this type have been reported repeatedly.

(7) For a definition see: (a) Newton, C. G.; Ramsden, C. A. *Tetrahedron* **1982**, *38*, 2965−3011. (b) Ollis, W. D., Stanforth, S. P., Ramsden, C. A. *Tetrahedron* **1985**, *41*, 2239−2329.

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(10) As reported for *o*-phthaldialdehyde: Powell, M. R.; Rexford, D. R. *J. Org. Chem.* **1953**, *18*, 810−814. This method is superior to the procedure described in the patent literature,[11] as the amount of the corresponding bisacetal was only small.

(11) Jpn. Kokai Tokkyo Koho JP 81.156.229 (Dec. 2, 1981); *Chem. Abstr.* **1982**, *96*, 142458m.

(12) This methodology has been worked out by A.-C. Koch: Ph.D. Dissertation, University of Kiel, 1991.

(13) (a) Kappe, T. *Encyclopedia of Reagents in Organic Synthesis;* Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 1, 557−579. (b) Kappe, T.; Lube, W. *Monatsh. Chem.* **1971**, *102*, 781−787. (c) Friedrichsen, W.; Schmidt, R.; van Hummel, G. J.; van den Ham, D. M. W. *Liebigs Ann. Chem.* **1981**, 521−531.

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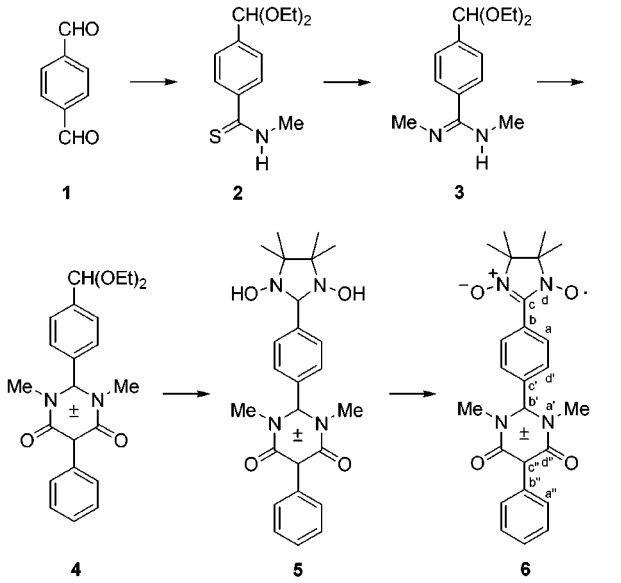
complished with lead dioxide (DMF, rt) to give **6** as dark bluegreen crystals with mp 238 °C (54%)[14] (Scheme 1).

Scheme 1



An X-ray crystal structure determination[15] revealed that in line with expectation the molecule is not planar. Torsion angles between the rings are determined as ϑ(a−b−c−d) = ϑ_1 = 38.51° (39.93°), ϑ(a′−b′−c′−d′) = ϑ_2 = 68.71° (69.98°), ϑ(a″−b″−c″−d″) = ϑ_3 = 52.04° (51.80°).[16] Values calculated by semiempirical methods (AM1, PM3)[17] differ considerably (AM1, ϑ_1 = 29.6°, ϑ_2 = 87.4°, ϑ_3 = 35.0°; PM3, ϑ_1 = 70.5°, ϑ_2 = 90.3°, ϑ_3 = 67.3°) although one should keep in mind a variation of $\Delta H_f°$ with δ_1 in compound

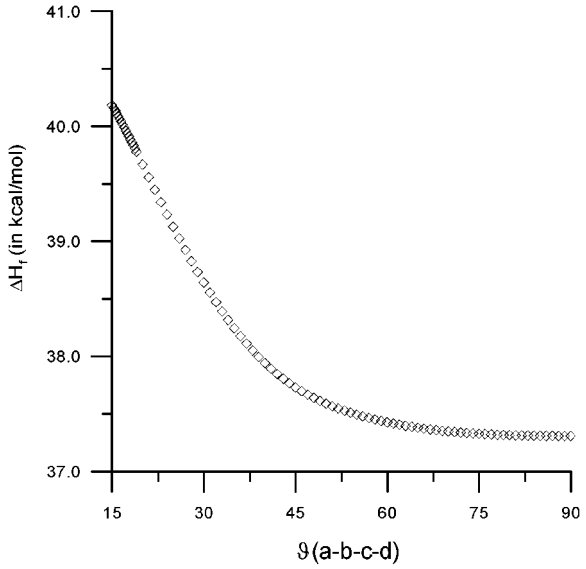
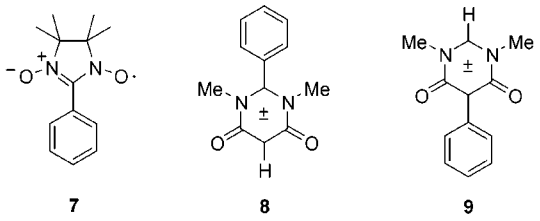


Figure 1. ΔH_f as a function of ϑ (a−b−c−d) for **7** (PM3 values).

7 is only small (see Figure 1). The same holds for $\Delta H_f° = \Delta H_f°(\vartheta_3)$ for compound **9** (rotational barrier, 2.9 kcal/mol (PM3)), whereas the rotational barrier ($\Delta H_f° = \Delta H_f°(\vartheta_2)$) in **8** is high.[18]



The synthetic methodology described in this paper has also been extended to the preparation of other NIT radicals with a pyrimidiniumolate group.[19] Magnetic measurements of **6** and related compounds[20] will be reported in due course.

Acknowledgment. The continuous support of our work by The Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Experimental procedures and IR, UV, ^{1}H NMR, ^{13}C NMR, and MS for compounds **2**−**5.** This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) On the basis of spectroscopic evidence, including EI-MS. The structures of all new compounds were unequivocally authenticated (see Supporting Information).

(15) X-ray data for **6**: $C_{25}H_{27}N_4O_4$, M_r = 447.51, orthorhombic, a = 9.919(3), b = 10.921(1), c = 20.876(6), V = 2261.2 Å^3, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.315 gcm^{-3}, μ(M$_o$ K$_\alpha$) = 70.073 pm, crystal dimensions 0.6 × 0.5 × 0.1 mm^3 (slow evaporation of ethyl acetate). Data were measured at room temperature on a PW-1100 4-circle diffractometer. R1 for 1906 $F_o > 4\sigma(F_o)$ = 0.0483 wR2 for all 2445 independent reflections = 0.1474 (F_o). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 145335. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, U.K. Fax: +44-(0)1223-336033. Email: deposit@ccdc.cam.ac.uk.

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(19) Greve, S.; Friedrichsen, W.; unpublished material. Part of the Ph.D. Dissertation of Greve, S., University of Kiel, 2000.

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