PERKIN 2

Structural and electrochemical properties of a novel N,N'-dialkyl-substituted quinone diimine

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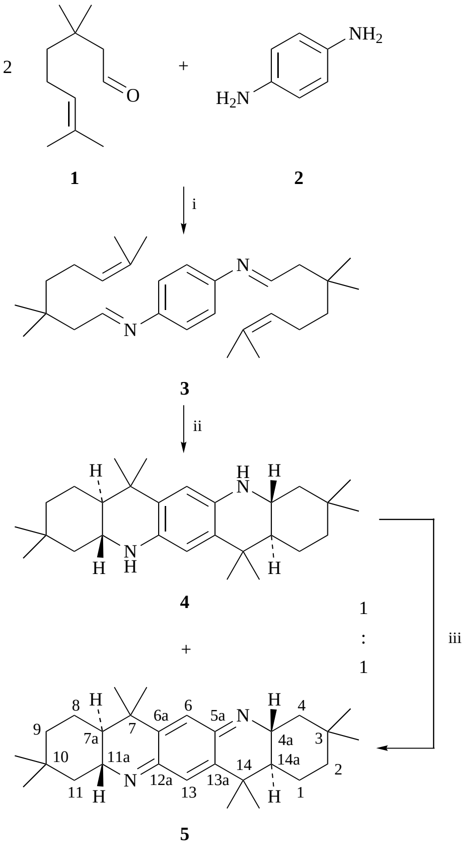
***trans*,*trans*-3,3,7,7,10,10,14,14-Octamethyl-1,2,3,4,4a,7,7a,8,9,10,11,11a,14,14a-tetradecahydroquino-[2,3-*b*]acridine 5, formed by a Lewis acid-catalyzed biscyclization of *N*-arylbisimine 3 and subsequent autoxidation, represents the first stable example of the unexplored class of N,N'-dialkyl-substituted quinone diimines. The X-ray crystal structure of 5 exhibits the following features: space group $P2_1/c$; a ribbon-like arrangement of two parallel strands along the *b*-axis. The smallest intermolecular distance between two quinoid systems is 4.846 Å and therefore any close aromatic contacts in this material can be precluded. A chemically reversible single electron reduction at $E^0 = -1.87$ V has been observed by cyclic voltammetry.**

Introduction

Interest in quinoid systems has been stimulated by the reversible redox properties[1] and possible applications as organic conducting materials.[2] Although numerous quinone diimines[3] with electron-withdrawing substituents on nitrogen (*e.g.* CN, SO_2R, CO_2R)[4] are known, their aliphatic counterparts remain largely unexplored.[5] Only the N,N'-dimethyl-[6] and N,N'-dicyclohexyl-substituted quinone diimines[7] have been described, and both seemed to be rather unstable. During our ongoing studies on formal hetero-Diels–Alder reactions of *N*-arylimines, we recently obtained pentacyclic N,N'-dialkyl-substituted quinone diimine **5** as an unexpected by-product together with the diamine **4** by a Lewis acid-induced biscyclization of the bisimine **3** (Scheme 1).[8] In contrast to the diamine **4**, whose formation can be rationalized by a stepwise mechanism *via* cyclization of an iminium ion followed by a subsequent Friedel–Crafts-type cyclization of the tertiary carbenium ion and tautomerization to the hexadecahydroquino[2,3-*b*]acridine **4**,[9] the mechanism of the formation of quinone diimine **5** under these conditions remained unclear. Encouraged by its remarkable stability we therefore investigated quinone diimine **5** in more detail with respect to the synthesis, structural and electrochemical properties. The results are described below.



Scheme 1 *Reagents and conditions:* i, molelcular sieves 4 Å (powder), CH_2Cl_2, 25 °C, (99%); ii, $MeAlCl_2$ (2.5 mol equiv.), CH_2Cl_2, −78 °C, then 25 °C, 2 days (95%); iii, O_2, CH_2Cl_2, 25 °C, 1 day (87%)

Results and discussion

As mentioned previously,[8] treatment of bisimine **3** (prepared from 3,3,7-trimethyloct-6-enal **1** and *p*-phenylenediamine **2**) with $MeAlCl_2$ in anhydrous dichloromethane gave a (52.6 : 47.4) mixture of diamine **4** and quinone diimine **5**, which could be separated by preparative HPLC. Despite carrying out the cyclization under rigorously deoxygenated conditions, we suspected that quinone diimine **5** was formed *via* autoxidation from **4** during aqueous work-up.[3] Therefore a solution of **4** in dichloromethane was stirred in an open flask. After one day complete conversion was observed and the quinone diimine **5** was isolated in 87% yield. Following this protocol **5** can be conveniently prepared from **3** without the tedious chromatographic separation of **4** and **5** by direct autoxidation of the crude cyclization mixture. However, compound **5** might have been formed, at least partially, *via* a radical cation-induced mechanism, because it is known that aluminium Lewis acids like $AlCl_3$ in dichloromethane or chloroform can be used as oxidizing agents for π-systems[10] and can induce radical cation formation.[11] In order to rule out this hypothesis, bisimine **3** was cyclized in the presence of 2.5 mol equiv. of MeAlCl$_2$ and either 0.1 mol equiv. of dibenzoyl peroxide or 0.1 mol equiv. of galvinoxyl respectively. Neither the radical starter nor the inhibitor caused any change of the product ratio **4**:**5**. This result strongly supports the mechanism of autoxidation during work-up.

Fortunately, an X-ray crystal structure of **5** could be obtained (Fig. 1). *trans*,*trans*-3,3,7,7,10,10,14,14-Octamethyl-1,2,3,4,4a,7,7a,8,9,10,11,11a,14,14a-tetradecahydroquino-[2,3-*b*]acridine **5** crystallized from hexane–ethyl acetate as yellow monoclinic needles of the space group $P2_1/c$.[12,13] Within the limits of error the molecular geometry strongly supports the proposed D_{2h} ($2/m$ $2/m$ $2/m$) symmetry. The observed bond lengths of the quinoid system (N5–C5A–C6–C6A–C12A–N12–C13–C13A) are very similar to those of *N*,*N*′-dicyano-substituted quinone diimines.[14,15] Only the C=N bond [1.290(2) Å] of **5** is slightly shortened by 0.03 Å as compared to 1.320(5) Å in *N*,*N*′-dicyano-2,5-dimethylquinone diimine.[14] This difference is probably caused by the decreased bond order in the dicyanoquinone diimines due to the conjugation of the C=N bond with the -*M*-substituted imine moiety. A view of the packing diagram along the *c*-axis shows a ribbon-like, twisted orientation of quinone diimine **5** along the *b*-axis (Fig. 2). However, a different perspective shows, that the ribbon actually consists of two different strands of quinoid systems **5** (Fig. 3). Two quinone diimines **5** within one strand are related by a crystallographic translation along the *b*-axis. Within different strands two molecules of **5** are related by a crystallographic C_2-axis. The closest contact between the centres of two quinoid systems is 7.618 Å. As can be seen from Fig. 4, the shortest possible π–π-distance is 4.848 Å, which is the distance between the C=N groups of two neighbouring quinone diimines **5**. That means stabilizing effects caused by π–π-stacking are certainly not operative in this system.

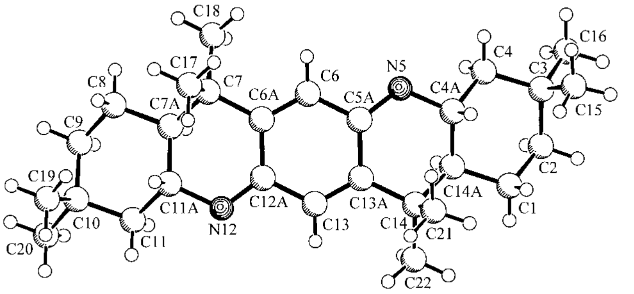


Fig. 1 X-Ray crystal structure of quinone diimine **5**. Selected bond lengths/Å: N5–C5a, 1.290(2); C5a–C6, 1.464(2); C6a–C6, 1.335(2); C6a–C12a, 1.474(2); C12a–N12, 1.290(2); C12a–C13, 1.465(2); C13–C13a, 1.340(2); C5a–C13a, 1.473(2). Selected angles/°: C5a–C6–C6a, 123.77(14); C6–C6a–C12a, 118.34(14); C6a–C12a–C13, 117.54(14); C12a–C13–C13a, 124.28(14); C13–C13a–C5a, 117.73(14); C13a–C5a–C6, 118.08(13).

Cyclic voltammetric measurements of compound **5** showed a chemical reversible single-electron reduction at $E^0 = -1.87$ V in THF (Fig. 5).[16] The reduction peak was observed at -1.93 V and the corresponding oxidation peak at -1.81 V.[17] The negative redox potential illustrates the weak oxidizing properties of compound **5** in comparison with -*M*-substituted quinone diimines, whose E^0 values are typically in the range between $+0.8$ V and -0.5 V.[18] The E^0 value of **5** is even below those found for quinones (between $+0.2$ V and -1.5 V). However, with respect to potential applications in molecular electronics and the design of new charge transfer complexes, it might be desirable to have a system with reversible redox behavior in a low potential range that is otherwise not accessible.

Experimental

General experimental conditions

These are reported elsewhere.[8] Syntheses and spectroscopic data for bisimine **3**, diamine **4** and quinone diimine **5** were described previously.[8]

trans,*trans*-3,3,7,7,10,10,14,14-Octamethyl-1,2,3,4,4a,7,7a,8,9,10,11,11a,14,14a-tetradecahydroquino[2,3-*b*]acridine 5 *via* biscyclization-autoxidation

To a cooled solution of bisimine **3** (816 mg, 2.00 mmol) in anhydrous dichloromethane (25 cm^3) was added dropweise MeAlCl$_2$ (5.0 cm^3, 5.00 mmol; 1.0 mol dm^{-1} solution in hexane) at −78 °C under argon over a period of 1 h. The cooling was removed and the mixture was stirred for 2 days at room temperature. Then the mixture was poured into ice-cold 2 mol dm^{-3} aqueous NaOH (50 cm^3) and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 50 cm^3) and the combined organic layers were dried over sodium sulfate

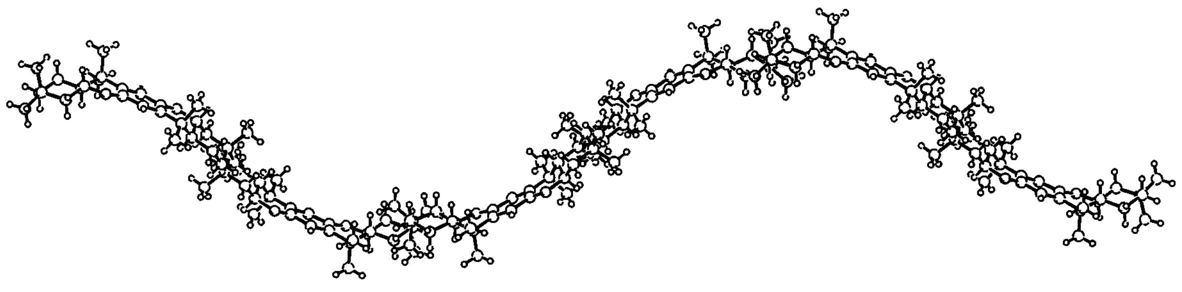


Fig. 2 Section of the X-ray crystal structure of **5** viewed along the *c*-axis

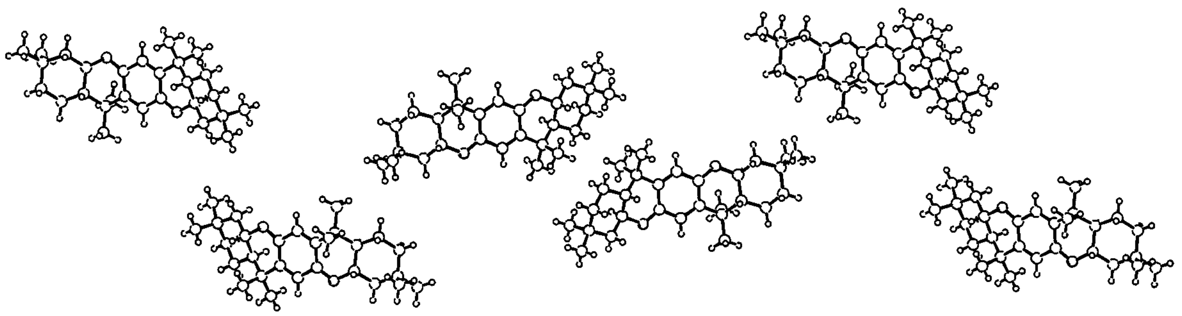


Fig. 3 Section of the X-ray crystal structure of **5** viewed along the *a*-axis

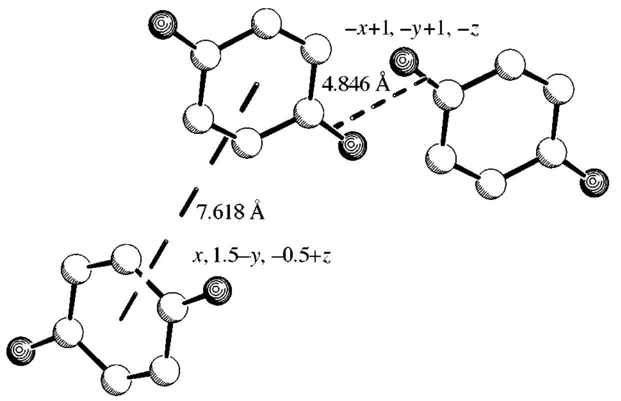


Fig. 4 Shortest π–π-distances (Å) within the X-ray crystal structure of **5**. The corresponding symmetry codes are also shown.

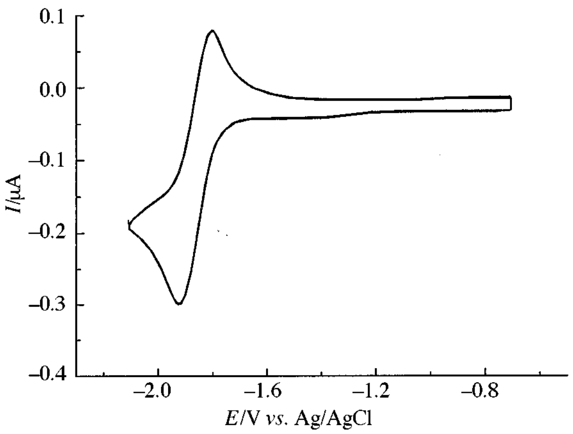


Fig. 5 Cyclic voltammogram of **5** in THF at 243 K (scan rate 100 mV s^{-1})

and filtered. The filtrate, which contained a mixture of **4** and **5** (52.6 : 47.4, determined by analytical HPLC) was vigorously stirred in an open-flask for 1 day. The solvent was evaporated and the residue was recrystallized from hexane–ethyl acetate (90 : 10) to give *yellow crystals* (674 mg, 83%); mp 304 °C. Spectroscopic data were in accord with ref. 8 (Found: C, 82.67; H, 10.42; N, 6.91. $C_{28}H_{42}N_2$ requires C, 82.70; H, 10.41; N, 6.89%).

Acknowledgements

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12 Details of the X-ray crystal structure determination of **5**: formula $C_{28}H_{42}N_2$, *M* 406.64, crystal size 0.40 × 0.35 × 0.10 mm, $a = 11.728(2)$, $b = 14.466(2)$, $c = 14.411(2)$ Å, $\beta = 93.14(1)°$, $V = 2441.3(6)$ Å^3, $D = 1.106$ g cm^{-3}, $m = 4.7$ cm^{-1}, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), Enraf-Nonius-CAD4 diffractometer, $T = -50$ °C, $l = 1.541\ 78$ Å, ω–2θ-scan, 5178 reflections collected, $(\pm h, -k, +l)$, $[\sin\theta/\lambda]_{\max.}$ 0.62 Å^{-1}, 4972 independent and 3946 observed reflections [F $4\sigma(F)$], 280 refined parameters $R = 0.053$, $\omega R^2 = 0.159$, largest difference peak and hole 0.37 and −0.25 e Å^{-3}, H atoms calculated; structure solved by direct methods (SHELXS-86);[13] refinement (SHELXL-93). Atomic coordinates, bond lengths and angles, and thermal parameters 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*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/94
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16 Details of the cyclic voltammetric experiment: the experimental set-up for the electrochemical investigations consisted of a typical three-electrode configuration. The working electrode was a Pt-disk (diam. 1 mm) sealed in soft glass, the counter electrode was a Pt-wire and the reference electrode an Ag-wire coated with AgCl. The voltammetric measurements were carried out with an AMEL 533 potentiostat and an EG&G/PAR scan generator Model 175. All experiments were performed under superdry conditions in an argon atmosphere. Tetrahydrofuran and tetrabutylammonium hexafluorophosphate were used as solvent/supporting electrolyte.
17 The purity of the quinone diimine **5** could be easily checked by CV. As soon as **5** contains traces of the corresponding hexadecahydroquino[2,3-*b*]acridine **4**, an additional smaller redox wave was observed at −0.14 V. The CV curve, which is shown in Fig. 5, contains no further signals beyond −0.8 V.
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