Helicene Dianions: The Effect of Charge on the Barrier to Racemisation
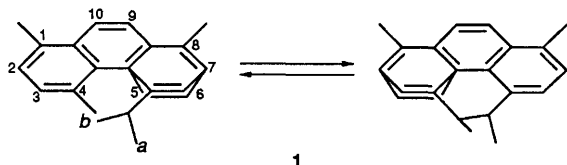
Ron Frim, Gil Zilber and Mordecai Rabinovitz*

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

The reduction of the polycyclic helicene 5-isopropyl-1,4,8-trimethylphenanthrene yields a $4n\pi$ conjugated dianion which preserves its helicity despite the decreased barrier to racemisation.

The smallest polycyclic molecule with an enforced helical structure[1] is a three-ring system, namely, phenanthrene substituted at the 4 and 5 positions.[2] Such chiral systems can be resolved into stable enantiomers if the barrier to racemisation is sufficiently high. The reduction of these hydrocarbons with alkali metals can, in principle, give paratropic $4n\pi$ dianions.[3]

We have previously studied the reduction products of $(4n + 2)\pi$ helicenes and found that the geometrical parameters of the parent systems are modified as a result of the formation of the respective dianions.[4] These studies were based on theoretical calculations and the degree of paratropicity. However, this was the first and only study which had taken into account the effect of the potential nonplanarity of such systems on their spectroscopic parameters. A comparison of the thermodynamic and kinetic parameters of the neutral system with those of the anions would provide an insight into the changes which occur in the parent helicene upon charging. The system of choice for such a study was the 5-isopropyl-1,4,8,-trimethylphenanthrene 1,†‡ a helicene which has a stereochemical marker, *i.e.* an isopropyl group in which the two methyl groups (*a* and *b*) are diastereotopic. These sites interchange *via* the racemisation process, due to a change in the sense of helicity. Therefore, in a slow racemisation process two separate ^{1}H NMR doublets for the two diastereotopic methyls are expected. Indeed, we see two doublets which appear at δ 1.6 and 0.56 (*J* 6.6. Hz).† At elevated temperatures, these diastereotopic groups are expected to become homotopic and the thermodynamic and kinetic parameters can be deduced.[5,6] The neutral system was prepared *via* a modified Wittig reaction.†‡ The anion was prepared by reduction of 1 with lithium or sodium metal.‡ The racemisation process of 1 is very slow indeed (in the NMR time scale) and no significant changes in the proton spectrum were observed up to a temperature of 435 K. We therefore resorted to the saturation spin transfer method.[7] The experiment was

carried out at 387 K with a selective 180° pulse on the methyl line at δ 0.56 followed by a non-selective 90° rf pulse.§

The result of a series of such experiments is shown in Fig. 1. It is clear from this Fig. that the irradiation of one of the diastereotopic methyl groups affected the ^{1}H NMR line intensity of the other. From this dependency we calculated the rate constant for the racemisation process.§ Introducing this rate constant into the Eyring equation gives $\Delta G^{\ddagger}$ value of 22.2 kcal mol^{-1} (1 cal = 4.184 J) for the racemisation process.

Structural characteristics of the neutral species were calculated using the molecular mechanics MMX force field method based on MM2 and MMPI programs developed by Allinger[8]¶ (Fig. 2). The most important structural parameter obtained from these calculations is the twist angle θ of the bay region. This dihedral angle of C(4)–C(4a)–C(4b)–C(5) is 38.34°. It can be seen from the molecular mechanics calculations that a coplanar configuration of the bay region of 1 does not permit the methyl group at the 4 position and the isopropyl at the 5 position to exchange positions. (This coplanar transition state for racemisation requires a calculated free energy for racemisation of *ca.* 36 kcal mol^{-1}.) We therefore conclude that the transition state involves complex movements. The reduction product, *i.e.* the $4n\pi$-electron dianion may undergo, in principle, geometric changes.[9] However, this dianion can adopt a planar structure thus allowing a better delocalization, and on the other hand charge separation may end up with a
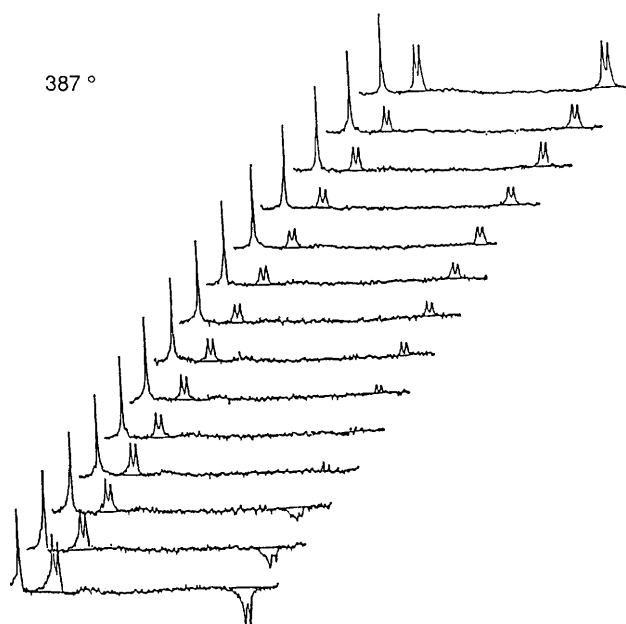

1

387 °

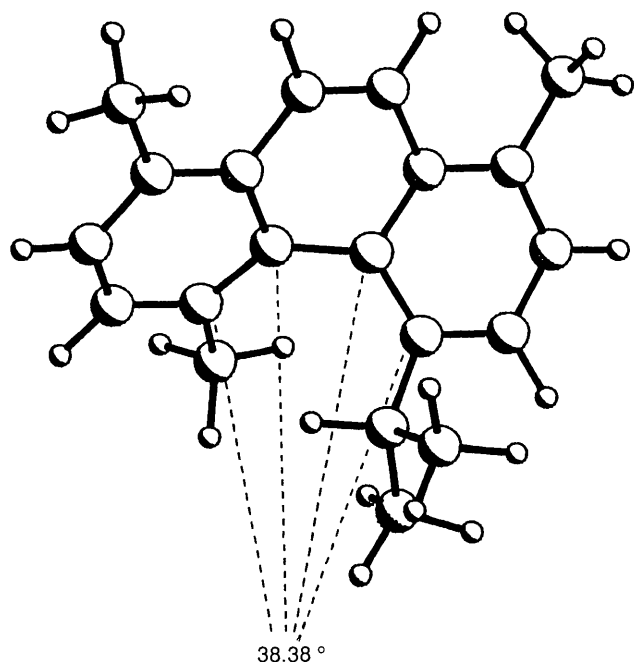**Fig. 1** ^{1}H NMR saturation transfer experiment of 1

Fig. 2 Spatial structure of **1** obtained from molecular mechanics calculations

twisted structure. The new charged system has a new frontier orbital due to the filling of an antibonding orbital of the neutral system. This process may result in elongation of carbon–carbon bonds.

The ¹H NMR spectrum of this dianion shows a nonplanar asymmetric dianion.‡ The lithium salt of the dianion (1^{2-} – 2Li⁺) shows a well resolved ¹H NMR spectrum at room temperature, due to its quenched paratropicity.[4] The two diastereotopic methyls of the isopropyl groups show two

separate doublets at δ 0.42 and 0.54 (*J* 3.9 Hz).‡ Raising the temperature shows a coalescence of these doublets and from the Gutowsky–Holm approximation,[6] we extracted the rate constant for the racemisation. From the Eyring equation[6] we calculated the free energy barrier ($\Delta G^{\ddagger}$) for racemisation of 15.4 kcal mol⁻¹. One cannot raise the temperature in order to arrive at the fast exchange region due to the sensitivity of the anion to elevated temperatures. This observation can be rationalized by the elongation of the C(9)–C(10) bond, *i.e.* 1.3657 Å in the neutral system *vs.* 1.4395 Å in the dianion (ωβ calculations).

In conclusion, this new nonplanar paratropic polycyclic dianion enabled the first study of the structural dynamic behaviour of a charged helicene dianion. It is clear that upon charging, the electronic structure induces a change in the barrier of the nonplanar dianion. Despite the decreased barrier, the helicity is maintained in the dianion.

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