Photoinduced Selective N.M.R. Line Broadening Effects in Polycyclic Aromatic Dianions. N.M.R. Identification of Radical Monoanions as Primary Photoproducts

Ron Frim,[a] **Mordecai Rabinovitz,**[a*] **and Karol A. Muszkat**[b*]

[a] *Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
[b] *Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel*

Polycyclic dianions, *e.g.* dibenzo[*a,c*]tetracene, undergo an electron photoejection process and form radical anions which induce n.m.r. line broadening by electron exchange with the paramagnetic photointermediate.

We report direct n.m.r. evidence establishing that radical anions $A^{\cdot-}$ are the primary products of the electron photoejection process of aromatic polycyclic dianions, A^{2-} [reaction (1)]. This process, and the reverse ground-state recombination (2), were examined extensively by both static[1,2] and time resolved[3] optical spectroscopy techniques.

$$A^{2-} \xrightarrow{h\nu} A^{\cdot-} + e^- \qquad (1)$$

$$A^{\cdot-} + e^- \longrightarrow A^{2-} \qquad (2)$$

We have explored these processes by searching for selective laser-photoexcitation induced ^{1}H n.m.r. line broadening effects[4] due to the photo-ejection step (1) and the reversal of line broadening, due to step (2). Our n.m.r. results identify the paramagnetic radical monoanion $A^{\cdot-}$ positively as the primary photoproduct, and establish the complete chemical reversibility of the cycle (1) + (2).

Line broadening due to instantaneous heating of the sample as a result of the light pulse does not occur. This was shown by variable temperature blank experiments.

The selective photoinduced proton n.m.r. line broadening effects at 300 MHz (Figure 1) in the dibenzo[*a,c*]tetracene (DBT) dianion[5] are characteristic of nuclear relaxation due to fast electron exchange of a diamagnetic molecule D (the dianion) with an isonuclear paramagnetic species P (the radical monoanion) [process (3)].[6] The identification of the

$$D + P \longrightarrow P + D \qquad (3)$$

paramagnetic photointermediate rests on its unpaired electron distribution (*cf.* Figure 2) as deduced from the magnitude of its line broadening.[4] Thus, in the n.m.r. spectrum of DBT^{2-}, the strongest photoinduced line broadening effects (see Figure 1, B and C) are shown by signals a, b, c, and d due to the anthracene subunit protons (9—16-H; *cf.* Figure 2).[5] Within this subunit, the larger effect is observed in signals a (9- and 10-H) and b (15- and 16-H). The effects observed in the phenanthrene subunit (signals e—h, corresponding to protons 1—8-H, *cf.* Figure 2) are much smaller than those observed in the anthracene subunit. In the former subset some residual *J* coupling structure is still observed, even at the higher light dose (Figure 1c). This selective pattern reflects the distribution of the unpaired spin density, ρ, in the DBT monoanion given in Figure 2.

From the above, a line broadening effect due to the exchange contribution of process (1) to the transverse relaxation time in the weak pulse limit expression[6] is as

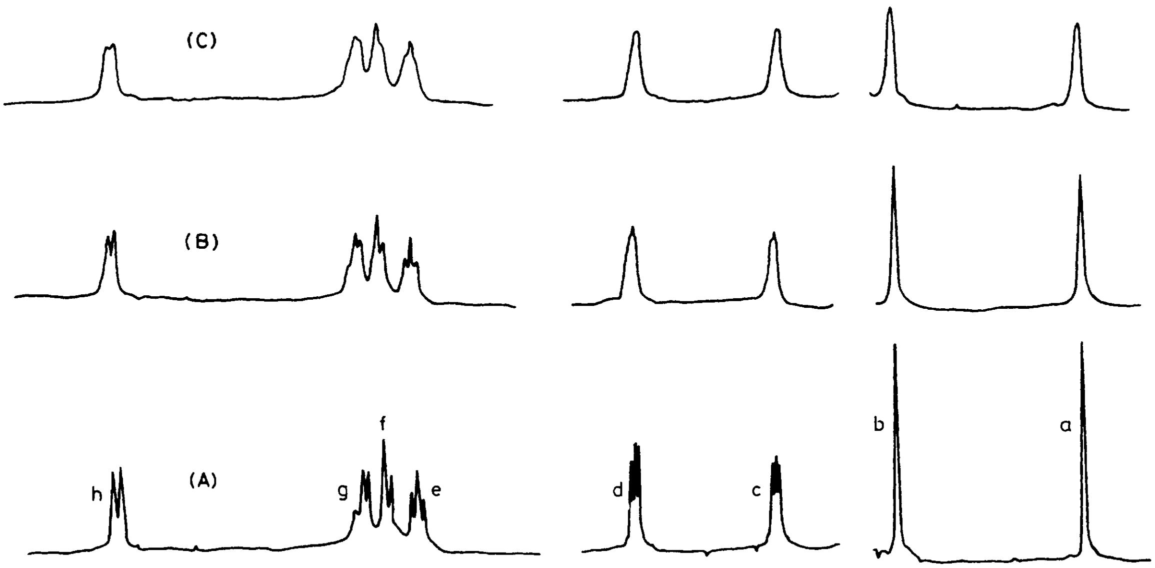

Figure 1. Dibenzo[*a,c*]tetracene dianion, as disodium salt. 300 MHz ^{1}H n.m.r. spectra of [$^2H_8$]tetrahydrofuran solution, 0.05 M, vacuum sealed; 5 mm diameter sample cell. Spectra obtained at 298 K by acquisition of 8 scans on a CXP-300 Bruker spectrometer. (A) Dark spectrum; (B) light spectrum. Each scan is preceded by through-coil excitation (0.6 s duration) with the 514 nm line of an argon laser (Spectra Physics, model 2025; 3.6 W single line power) and followed by a 10 s thermal relaxation delay; (C) same as B but 1 s excitation period used. Assignment is as follows: a, 5-, 15-H, δ 2.7; b, 9-, 16-H, δ 3.45; c, 11-, 14-H, δ 4.12; d, 12-, 13-H, δ 4.68; e, 3-, 6-H, δ 6.45; f, 1-, 8-H, δ 6.57; g, 2-, 7-H, δ 6.66; h, 4-, 5-H, δ 7.63.

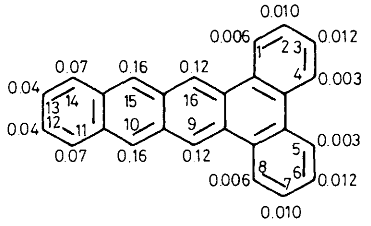

Figure 2. Dibenzo[*a*,*c*]tetracene, giving Hückel π M.O. unpaired spin densities (ρ) of radical monoanion $A^{\bullet -}$.

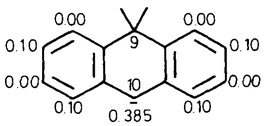

Figure 3. 9-Protonated anthracene radical ($AH^\bullet$), giving Hückel π M.O. unpaired spin densities (ρ).

expected from equation (4), where the hyperfine coupling factor a_i is related to ρ by the relationship (5).[7]

$$\Delta T_2^{-1} = a_i^2[P]/k[D]^2 \qquad (4)$$

$$a = -Q\rho \qquad (5)$$

In addition to DBT^{2-} we have also observed selective photoinduced n.m.r. line broadening effects in a number of other polycyclic aromatic dianions, *i.e.*, anthracene, tetracene, and acenaphthylene dianions. Thus, these effects seem to be general, as is the electron photo-ejection process of anions. In addition, line broadening was also observed in monoprotonated dianions, *i.e.* AH^- (Figure 3). Here the photoejection process leads to the reduced hydrocarbon radical $AH^\bullet$, by the process (6).

$$AH^- \xrightarrow{h\nu} AH^\bullet + e^- \qquad (6)$$

In the case of the anthracene monoprotonated dianion, we observe on 514 nm photoexcitation a large line broadening effect on the 10-H signal (singlet, δ 5.27). Indeed, C-10 is the largest unpaired spin density centre in $AH^\bullet$ (see Figure 3). The line broadening effects of the other signals are very much smaller, in agreement with the computed π M.O. unpaired spin density distribution in $AH^\bullet$.

In the previous studies,[1—3] in the absence of direct molecular structure evidence, the formation of aromatic polycyclic monoanion radicals on electron photoejection from the dianions [process (1)] was postulated on the basis of the indirect optical spectroscopy information then available. However, the missing evidence establishing the molecular identity of the labile photoproduct of process (1) is provided by the present selective photoinduced n.m.r. line broadening results.

The normal line width of dianion [(1)] and of AH^- signals is fully regained upon termination of excitation. In fact, the rate constant of process (2) can be estimated by interposing a variable recovery delay following laser excitation and preceding the r.f. pulse. Apparent half-time values of the order of 1 s are usually obtained.

The determination of the molecular structure of low concentrations of labile phototransients is still a difficult experimental problem. Nevertheless, both the present study and previous results on the primary photochemical event in chloropromazine[4] clearly show that selective photoinduced n.m.r. line broadening effects provide a generally applicable tool for the investigation of the molecular structure of trace amounts of paramagnetic photo-intermediates. Therefore, it is important to note the powerful amplification mechanism inherent in such application of selective photoinduced line broadening effects. This line broadening (as given by the weak pulse limit expression)[6] is detected, not in the signals of the paramagnetic species, present only in trace amounts, but in those of the diamagnetic substrate molecules present at much higher concentrations.

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