

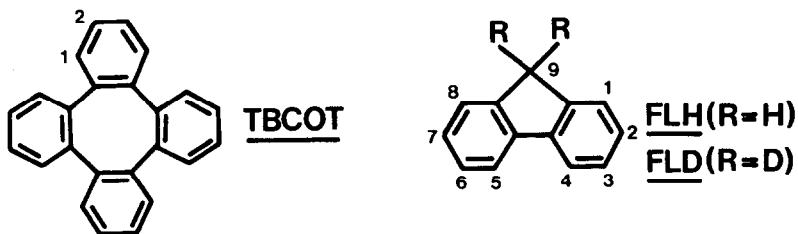
PHOTOCHEMICAL GENERATION OF RADICAL ANIONS.
AN ACCESS TO NOVEL STRUCTURES

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Abstract: The preparation of the radical anions of tetrabenzocyclooctatetraene (TBCOT) and fluorene (FLH) by photochemical methods leads to the observation of novel structures.

Ejection of an electron is one of the best documented light induced processes which occurs with carbanions in the condensed phase [1]. It is therefore quite surprising that this basic phenomenon is only poorly exploited for the preparation and ESR spectroscopic investigation of new paramagnetic hydrocarbon species [2]. This communication focuses the attention on two applications; to the preparation of a radical anion i) by the photooxidation of an electron richer species (TBCOT⁻) and ii) by the light induced electron transfer from a stable carbanion (FI⁻) to a neutral compound. The choice of the substrates has proven advantageous in dealing with new structures of the two alkali metal salts TBCOT⁻/K⁺, FLH⁻/Na⁺.



Photooxidation of TBCOT^{•-}: The ESR spectrum of TBCOT^{•-} in MTHF observed upon reduction of the neutral compound on a potassium mirror is very similar to that originally described in the literature [3]. The analysis yields two coupling constants (0.139, 0.020mT), each belonging to a set of eight equivalent protons. Upon further reduction, the ESR spectrum of TBCOT^{•-} disappears, due to the formation of TBCOT⁼ [4]. During irradiation of such a solution in the cavity of the ESR spectrometer [5], one observes again an ESR spectrum, the hyperfine structure of which substantially differs from that described above.

Nevertheless, this spectrum is assigned to the radical anion of TBCOT^{•-} for the following reasons: i) The ESR spectrum observed upon reduction of TBCOT exhibits the same width as that obtained upon photolysis of TBCOT⁼. ii) The analysis of the latter spectrum yields four coupling constants (0.171, 0.087, 0.022, 0.014mT), each associated with a set of four equivalent protons, whereby the averages of the two smaller (0.018mT) and of the two larger values (0.129) are comparable to the eight-proton coupling constants (0.020, 0.139mT) usually observed for TBCOT^{•-}. The fact that the ESR spectrum of TBCOT^{•-} immediately disappears when the light is cut off indicates that photolysis of the solution of TBCOT⁼ shifts the equilibrium (I) to the right.



Photoinduced electron transfer to FIH: It is well known that FIH^{•-} reacts to the diamagnetic anion FI⁻ by the loss of an hydrogen atom on C9. It is this process which impairs the ESR spectroscopic characterization of FIH^{•-} above approximately 200K. The irradiation of a mixture of FIH/FI⁻ (FI⁻ as sodium salt) in the cavity of an ESR spectrometer generates, however, a stationary concentration of FIH^{•-} which can be detected spectroscopically even at 280K. The formation of FIH^{•-} is certainly due to the photooxidation of FI⁻ followed by the capture of the ejected electron by FIH (see reaction scheme II). The fact that no ESR spectrum of FI[•] is observed might be rationalized by the dimerization of this neutral radical.

The photoinduced electron transfer was observed in several solvents. The most remarkable findings result from investigations in MTHF/benzene for which solvent the high- (260K) and the low-temperature spectrum (180K) significantly differ. The analysis of the low temperature spectrum yields five two-proton coupling constants (0.505, 0.414, 0.395, 0.123, 0.085mT) which are similar to those usually observed for FIH^{•-} [6]. The analysis of the high temperature spectrum yields two coupling constants (0.418, 0.330mT) of two single protons in addition to four two-proton coupling constants (0.504, 0.424, 0.129, 0.078mT). Investigation of FID^{•-} at 260K ensures the assignment of the two one-proton coupling constants to the protons on C9. The average of these two values (0.374mT) is close to the coupling constant (0.414mT) usually observed for the protons on C9 in FIH^{•-} [6]. The remaining two-proton coupling constants compare satisfactorily with the values of the α -protons of FIH^{•-} at low temperature (see Table).

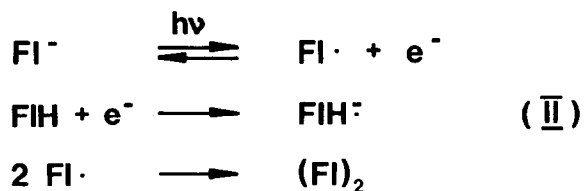


Table: Coupling constants of $\text{TBCOT}\dot{-}$ and $\text{FIH}\dot{-}$ in mT.

	$\underline{1}^a$		$\underline{2}^a$		
$\text{TBCOT}\dot{-}^b$	0.020		0.139		
$\text{TBCOT}\dot{-}^c$	0.022	0.014	0.171	0.087	
	$\underline{1,8}^a$	$\underline{2,7}^a$	$\underline{3,6}^a$	$\underline{4,5}^a$	$\underline{9}^a$
$\text{FIH}\dot{-}^d$	0.085	0.505	0.123	0.395	0.414
$\text{FIH}\dot{-}^e$	0.078	0.504	0.129	0.424	0.418 0.330

- a) Positions
 b) $\text{TBCOT}\dot{-}$ generated by direct reduction of TBCOT .
 c) $\text{TBCOT}\dot{-}$ generated by photooxidation of $\text{TBCOT}^=$.
 d) $T = 180\text{K}$
 e) $T = 250\text{K}$

Structural considerations: It has been reported previously that the symmetry of $\text{TBCOT}^=$ (C_2) is reduced with respect to that of the neutral compound (D_{2d}) [4]. This symmetry reduction is caused by a deformation of the molecular framework from the "tub"-type to a bis(biphenylene)-type structure and by a partial localization of the charge on two benzene rings. In view of these findings, the ESR data observed for $\text{TBCOT}\dot{-}$ upon photolysis of the dianion $\text{TBCOT}^=$ are not surprising. Obviously, the hyperfine data of this radical anion reflect the structure of the "parent" dianion and can be rationalized analogously by a deformation of the molecular framework and/or a polarization of the spin density by an unsymmetrically positioned counterion. This interpretation implicitly includes the assumption that the two different structures of $\text{TBCOT}\dot{-}$ which are accessible by different preparation methods (reduction of TBCOT ; photooxidation of $\text{TBCOT}^=$) are separated by an activation barrier impairing a fast interconversion.

The occurrence of a tight ion pair seems to provide a rationalization for the observed coupling constants of FIH^- at high temperatures. According to the π -charge distribution in FIH^- , sites of preferred association of the counterion are below and above the central five membered ring (in a close proximity of one proton on C9). Different coupling constants for the protons on C9 are observed when the migration of the counterion between the two sites is slow on the hyper-fine time scale. An analogous ion pair structure has been suggested for the pyracene radical anion [7].

Conclusion and outlook: The two examples discussed above demonstrate that photooxidation of a dianion and photoinduced electron transfer from a carbanion to a neutral species are convenient methods for the preparation of radical anions. The application of the former method is of special interest in the case where the dianionic but not the neutral species is available [2] or where the dianion spectroscopically differs from the neutral compound. The second method facilitates the preparation of unstable radical anions. Further applications of both techniques will be discussed in later publications.

This work was supported by the Swiss National Foundation. Financial assistance by Ciba-Geigy SA, Sandoz SA and F. Hoffmann-La Roche & Cie, SA, Basel is also acknowledged.

References:

- [1] G.J. Hoytink, P.J. Zandstra, *Mol. Phys.* 3, 371 (1960).
- [2] D. Wilhelm, J.L. Courtneidge, T. Clark, A.G. Davies, *J. Chem. Soc., Chem. Commun.* 1984, 810.
- [3] A. Carrington, H.C. Longuet-Higgins, P.F. Todd, *Mol. Phys.* 8, 45 (1964).
- [4] W. Huber, A. May, K. Müllen, *Chem. Ber.* 114, 1318 (1981).
- [5] The light stems from a water cooled Hg high pressure lamp (Philips SP 1000W). It is focussed in the cavity of an ESR spectrometer (Varian E3).
- [6] F. Gerson, B. Kowert, B.M. Peake, *J. Am. Chem. Soc.* 96, 118 (1974).
- [7] M. Iwaizumi, T. Isobe, *Bull. Chem. Soc. Japan*, 38, 1547 (1965).

(Received in Germany 6 September 1984)