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4-β-AMINOETHYLAMINO-1,2-(ETHYLENE-1',2'-DIAMINO)-ANTHRAQUINONE: A CONDENSATION PRODUCT OF ETHYLENEDIAMINE AND LEUCOQUINIZARIN

M. S. Simon and D. P. Waller

Polaroid Corporation, Cambridge, Massachusetts 02139

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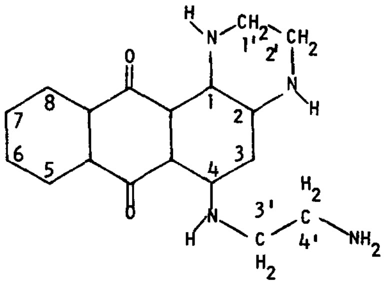
In an earlier publication (1) we called attention to differences between the visible absorption spectra of 1,4-bis(N-alkylamino)-anthraquinones and the spectra of a compound we believed to be 1,4-bis(β-aminoethylamino)anthraquinone. At that time we were unable to obtain satisfactory proton magnetic resonance spectra of this compound due to its low solubility in available solvents.

A recent publication by H. P. Kolliker and P. Caveng (2) which reported the facile ring closure of β-aminoethylamino-anthraquinone to 1,2(ethylene-1',2'-diamino)-anthraquinone, prompted us to reinvestigate the structural assignments in the 1,4-series.

The product of the condensation of leucoquinizarin with ethylenediamine was found to give a satisfactory proton magnetic resonance spectrum in deuterated dimethyl sulfoxide at 85°. This data is tabulated, and can be fully explained by the assumption that the condensation product is in fact 4-β-aminoethylamino-1,2(ethylene-1',2'-diamino)-anthraquinone (A).

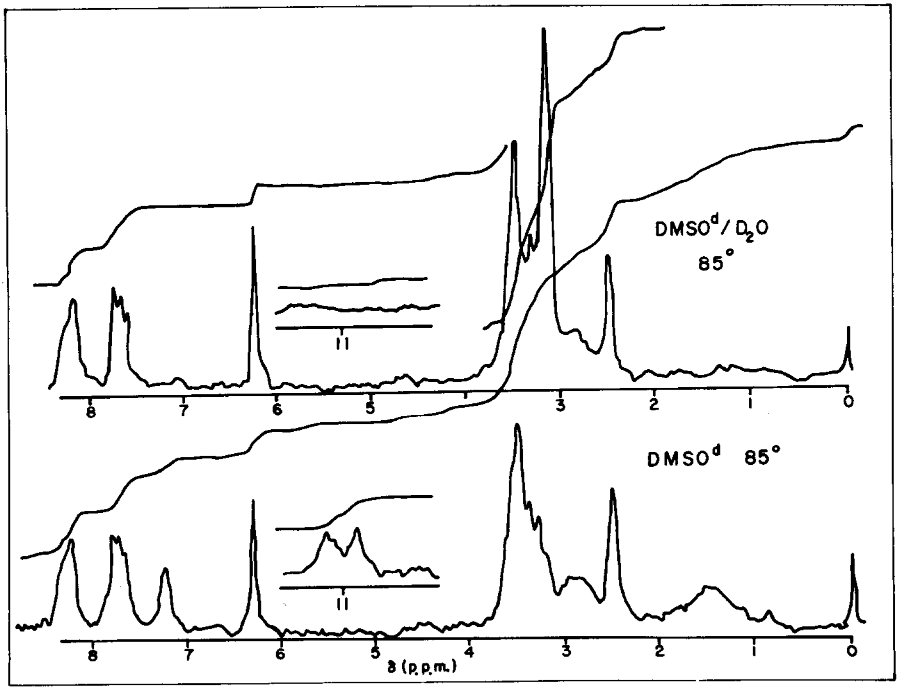


(A)

TABLE 1

ppm[1]	Multiplicity	No. Protons	Exchanged by D_2O	Assignment
11.18	s (br.)	1	yes	H on α-N (1 or 4)
10.84	s (br.)	1	yes	H on α-N (4 or 1)
8.16	m	2	no	H's at C-5 & C-8
7.64	m	2	no	H's at C-6 & C-7
7.16	s (br.)	1	yes	H on N at C-2
6.24	s	1	no	H at C-3
3.44	m	8	no	H's on C-1', C-2', C-3'
3.34				
3.24				
2.82	m (br.)			H on C-4'
1.4	s (br.)	2	yes	H's on N at C-4'

[1] TMS is the internal standard; DMSO peak is at 2.46 ppm, H_2O peak in exchange experiments is at 3.16 ppm.



The key evidence which we believe establishes this structure is: (a) only five aromatic protons are found, (b) the single aromatic proton is far upfield, at 6.24 ppm., showing that it is ortho to two amino substituents, (c) the material is unchanged by dissolving in DMSO at 85°.

This structural assignment offers a completely satisfactory explanation for the absorption spectra reported in the earlier publication. It is well known that electron donating substituents in the 2-position of 1,4-diaminoanthraquinones shift the absorption maxima to shorter wavelengths (3). Whereas 1,4-diaminoanthraquinone itself has its visible spectral peaks at 552 and 592 nm, 2-methoxy-1,4-diaminoanthraquinone absorbs at 534 and 573 nm, and 2-methylamino-1,4-diaminoanthraquinone at 537 and 576 nm. Moreover, the latter has a broad peak centering at 414 nm which corresponds to the short wavelength peak of 4(β-aminoethylamino)-1,2-ethylene-1',2'-diaminoanthraquinone (λ_{max} at 435, 563, 605 nm. All absorption spectra were taken in 2-methoxyethanol).

REFERENCES

(1) M. S. Simon, J. Am. Chem. Soc. 85, 1974 (1963).

(2) H. P. Kolliker and P. Caveng, Chimia 20, 281 (1966).

(3) See, e.g. Ko Naiki, J. Soc. Org. Synth. Chem., Japan 12, 185, 401 (1954); C.A. 51, 722b, g (1957).