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PREPARATION AND SPECTRAL CHARACTERIZATION OF SULPHUR-CONTAINING DIARYLAZO COMPOUNDS

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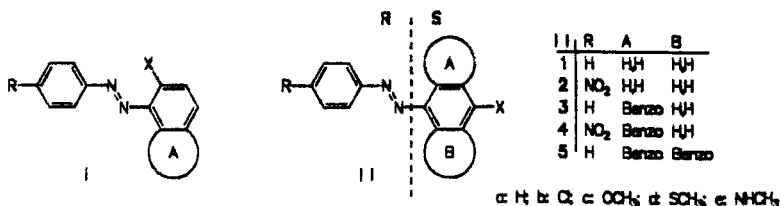
Abstract: By reaction of arylazo-substituted aryl halides with mercaptides, new arylazo-substituted arylsulfides are formed. These compounds are deeply coloured and exhibit an intense absorption band in the visible region, which can be reproduced quantitatively and interpreted satisfactorily by means of quantum chemical calculations in the framework of the PPP and LHM methods, respectively.

INTRODUCTION

Recently we have found a simple route for preparing 1-arylazo-substituted aryl sulphides starting from alkyl or aryl mercaptanes and arylazo-substituted chloro arylenes which have been accessible by a simple reaction of 1-arylazo-substituted phenols or naphthols with phosphorous chlorides in presence of DMF [1]. Very recently, this synthetic route could be extended to the preparation of several further types of mercapto-substituted diarylazo compounds, such as sulphur substituted oligoazo phenylenes, naphthylenes, and anthrylenes [2].

The new sulphur-containing azo compounds exhibit high thermal and photochemical stability, remarkable solubility in non polar or weakly polar organic solvents, and a deep colour, originating from an intense absorption band in the visible region. This absorption band shows a strong bathochromic shift with respect to the absorption maximum of the corresponding sulphur-free parent compound and to the chloro-substituted starting material. It is very close to the absorption band of the corresponding alkylamino-substituted arylazo compound.

In order to understand this rather unexpected spectral effect quantum chemical calculations using the well-elaborated PPP method [5] as well as the LHM method [6] have been performed considering the substituted diarylazo compounds 1- 5.



RESULTS

The results of the PPP calculations are summarized and compared to corresponding experimental data for the compounds studied in the following table. As can be seen, the experimental data can be satisfactorily described by this method for both the mercapto and the other substituted arylazo derivatives.

Measured Data					Calculated Data				
Nr.	λ_{\max}	(log ϵ)	ν	$\Delta\nu$	E	(log f)	ν	$\Delta\nu$	σ_D^e
1a	317 ^a	(4.34)	31.54	-	3.70	(0.09)	29.84	-	± 0.00
1b	324 ^a	(4.40)	30.86	68	3.66	(0.09)	29.51	33	+0.227
1c	342 ^a	(4.44)	29.23	231	3.46	(0.10)	27.93	191	-0.268
1d	362 ^a	(4.44)	27.62	392	3.40	(0.10)	27.42	242	-0.047
1e	380 ^a	(4.44)	26.31	523	3.27	(0.12)	26.37	347	-0.592
2a	331 ^a	(4.42)	30.21	-	3.63	(0.11)	29.27	-	+0.778
2b	327	(4.25)	30.58	37	3.60	(0.10)	29.03	24	
2c	370	(4.49)	27.03	318	3.40	(0.09)	27.42	185	
2d	407 ^b				3.33	(0.10)	26.88	239	
2e	437 ^a	(4.49)	22.88	733	3.20	(0.11)	25.81	346	
3a	372	(4.29)	26.88	-	3.24	(0.05)	26.17	-	
3b	375	(4.31)	26.66	22	3.21	(0.07)	25.90	27	
3c	392 ^a	(4.32)	25.51	137	3.06	(0.08)	24.69	148	
3d	433	(4.32)	23.20	368	3.00	(0.08)	24.27	190	
3e	447 ^c	(4.32)	22.37	451	2.90	(0.11)	23.36	281	
4a	389 ^a	(4.30)	25.70	-	3.71	(0.06)	25.08	-	
4b	392 ^a	(4.30)	25.51	19	3.07	(0.07)	24.76	32	
4d	511	(4.32)	19.56	614	2.59	(0.10)	20.88	420	
4e	529 ^a	(4.33)	18.90	680	2.39	(0.11)	19.27	581	
5a	445 ^b	(4.22)	22.47	-	2.70	(0.01)	21.78	-	
5b	450	(4.25)	22.22	25	2.67	(0.03)	21.59	19	
5c	452 ^d	(4.29)	22.12	35	2.61	(0.05)	21.05	73	
5d	472	(4.32)	21.18	129	2.55	(0.06)	20.57	121	
5e	482 ^d	(4.32)	20.74	173	2.54	(0.08)	20.49	129	

a) Ref. [7], b) Ref. [8], c) Ref [9], d) Ref. [10], e) Ref. [4]

Due to the results of the LHM method, which can reproduce the experimental data satisfactorily also, the observed bathochromic effect of alkylmercapto groups attached at arylazo chromophores results from two different effects, namely from a rather low ionization energy of the arylmercapto group, giving rise to a relatively low-energetic electron transfer configuration from the sulphur atom to the arylazo moiety, and from a relatively small coupling strength of the mercapto group to its adjacent aryl moiety, giving rise to a relatively low stabilization of the electronic ground state, but to a rather strong stabilization of the first electronic state of the alkylmercapto-substituted arylazo compounds studied.

REFERENCES

- [1] M. Schulze and H. Hartmann, Phosphorus, Sulfur, and Silicon, **61**, 161 (1991).
- [2] M. Schulze, H. Hartmann and E. Berthold, DD-Patent 289549 (1989); DD-Patent 287724 (1989).
- [3] H. Mustroph and J. Epperlein: J. Prakt. Chem., **327**, 49 (1985); H. Mustroph, Z. Chem., **25**, 385 (1985).
- [4] H.H. Jaffé, Chem. Rev. **53**, 191 (1953).
- [5] J.A. Pople, Trans. Faraday Soc., **49**, 1375 (1953); R. Pariser and R.G. Parr, J. Chem. Phys. **21**, 466 (1953).
- [6] J. Fabian, J. Signalaufzeichnungsmaterialien **6**, 307 (1978); Z., **67** (1979).
- [7] J. Fabian and H. Hartmann, Light Absorption of Organic Colorants (Springer, Berlin, Heidelberg, New York, 1980), p.42.
- [8] A. Burawoy and C. Turner, J. Chem. Soc., 469 (1950), 1286 (1952).
- [9] A.T. Peters, Dyes & Pigments, **8**, 99 (1987)
- [10] M. Nepras, M. Titz, M. Nenas, S. Lunac jr., R. Hridina and A. Lycka, Coll. Czech. Chem. Commun., **53**, 191 (1953).