Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 380–383

Photoinduced recoordination in the complexes of bis-aza-18-crown-6-containing dibenzylidenecyclobutanone with alkali and alkaline-earth metal cations

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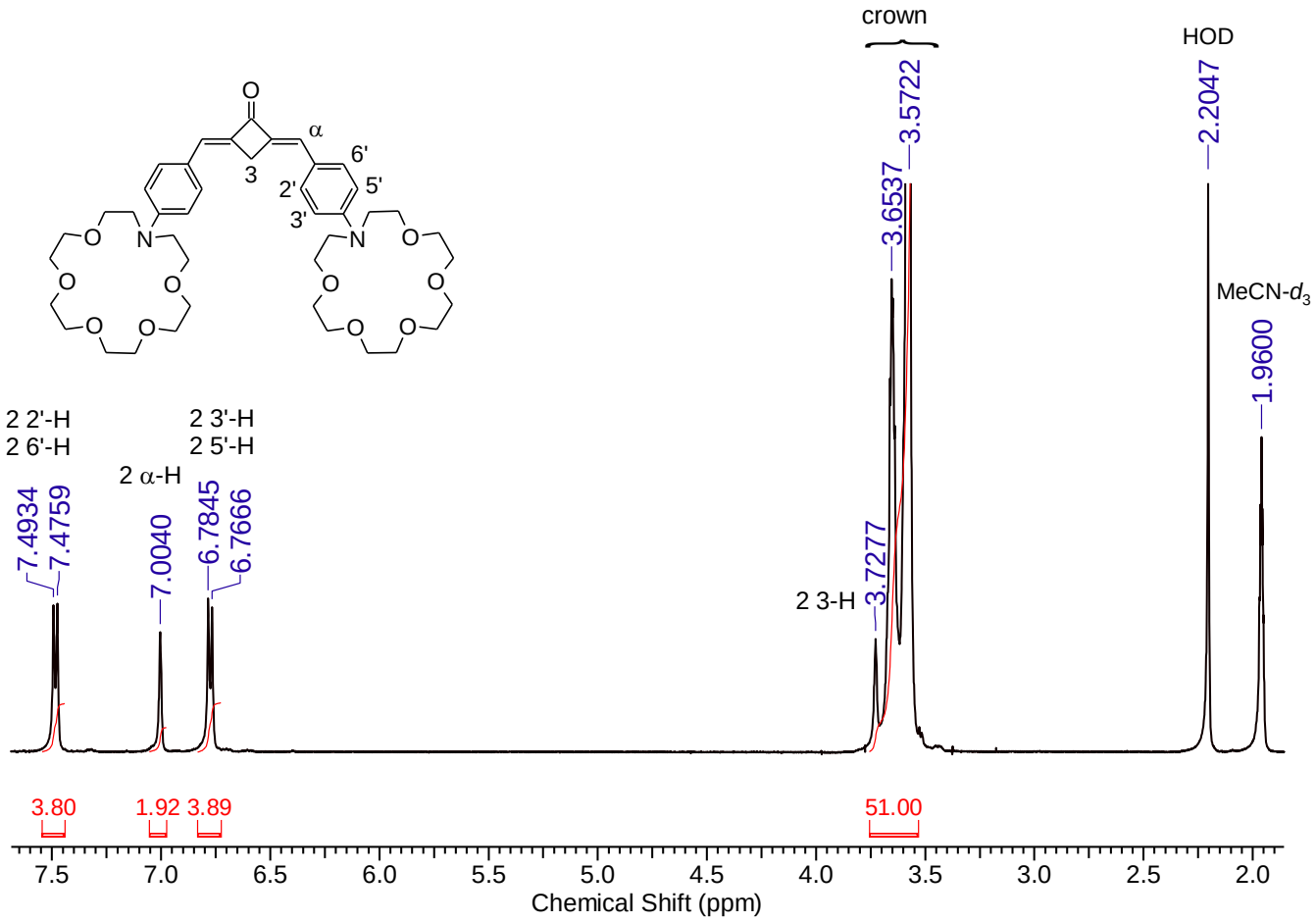


Figure S1 ^{1}H NMR spectrum of compound **1** in MeCN-d_3.

Details of quantum-chemical calculations

Quantum chemical calculations were performed using the GAMESS (US) program package with the 6-31G(d,p) basis set for carbon and hydrogen atoms, the 6-31G*(d,p) basis set for nitrogen and oxygen and the def2-SVP with the def2-ECP for barium.[S1] The geometry of the compounds in the ground state was optimized by means of DFT (BHHLYP functional). Absorption spectra were calculated by means of TDDFT (B3LYP functional). The environmental effects were included via the Solvation Model Density continuum model.[S2]

S1 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

S2 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem.* B, 2009, **113**, 6378.

Table S1 Calculated structural and spectral parameters of dye **1** and complexes (molecular fragment with atom numbers is shown below).

Parameters: r (Å), ψ (°), q (e.u.), λ, nm	**1**	**1**·$(Ba^{2+})_2$(ax)/(eq)	**1**·$(Ba^{2+})_2$·3$(MeCN)_2$ (ax)/(eq)	**1**·$(H^+)_2$
r (C_1–O)	1.208	1.197 / 1.200	1.200 / 1.202	1.226
r (C_1–C_2)	1.483	1.491 / 1.487	1.489 / 1.485	1.495
r (C_2–C_3)	1.334	1.331 / 1.331	1.331 / 1.332	1.345
r (C_3–C_4)	1.451	1.460 / 1.457	1.459 / 1.456	1.460
r (C_5–N)	1.386	1.438 / 1.411	1.445 / 1.402	1.485
r (N–Ba)	–	3.09	4.78	–
pyramidalization angle of N, ψ	10.0	27.7/11.4	–	24.6
charge of O (q, e.u.) (C=O(O))	–0.23 (–0.66)	–0.18 (–0.64)/ –0.21 (–0.66)	–	–0.14 (–0.43)
$\lambda_{\pi\rightarrow\pi^*1}$ (*f*)	484 (1.22)	387 (1.22)/ 447 (1.14)	–	355 (1.04)
$\lambda_{\pi\rightarrow\pi^*2}$ (*f*)	419 (0.23)	343 (0.28)/ 388 (0.27)	–	323 (0.13)
$\lambda_{n\rightarrow\pi^*}$ (*f*)	374 (0)	403 (0)/ 395 (0.00)	–	419 (0)

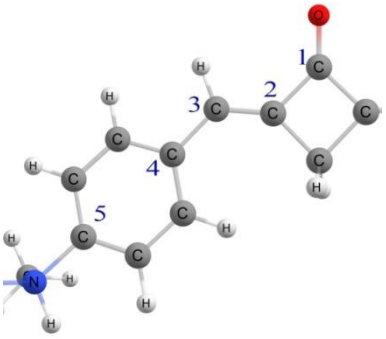
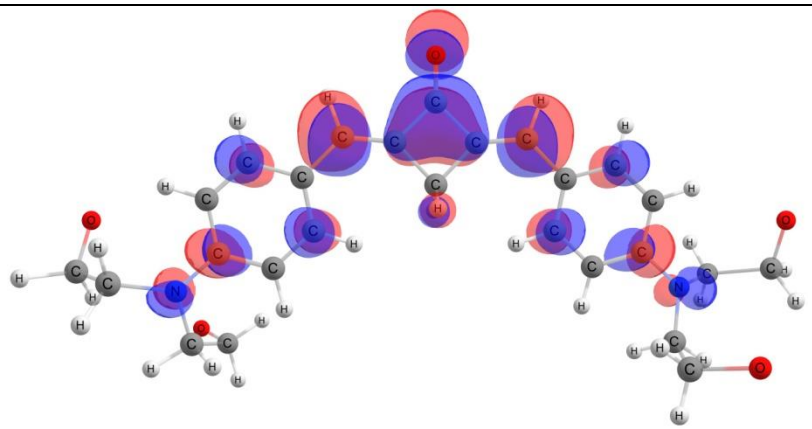
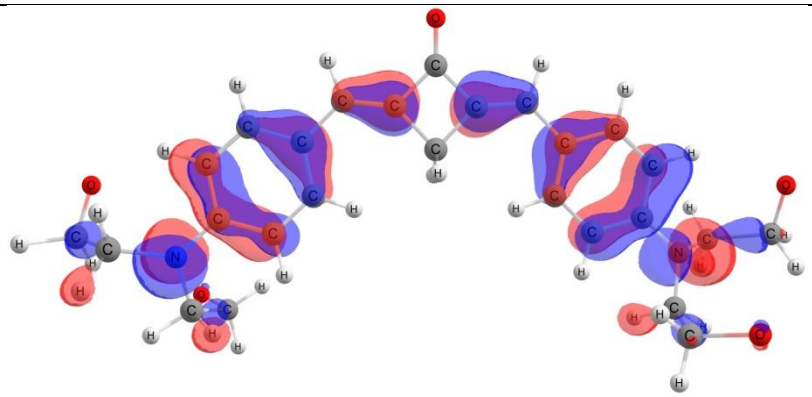
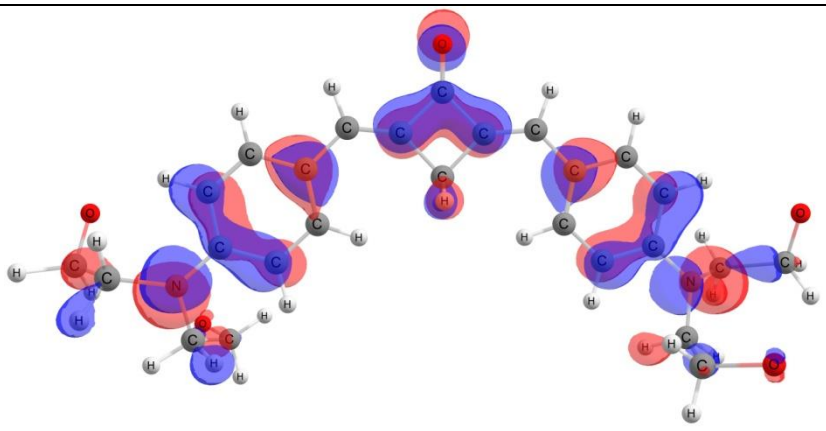


Table S2 Values of charges (by Mulliken) on atoms (groups) of dye **1**, calculated using DFT (S_0) and TD DFT (S_1) methods (molecular fragment with atom numbers is shown above).

Atoms (groups)	S_0	S_1	Δq (S_1-S_0)
C_1=O	–0.23	–0.503	–0.273
C_1	0.26	0.113	–0.147
O	–0.49	–0.616	–0.126
N	–0.445	–0.323	0.122

LUMO	
HOMO	
HOMO-1	

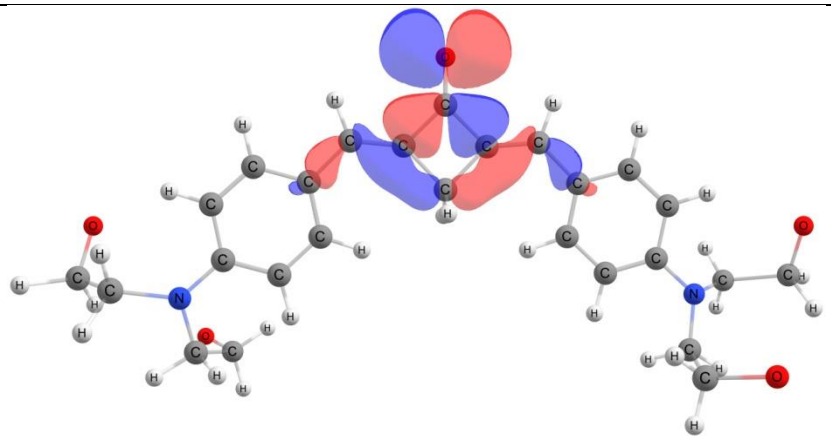
HOMO-2	

Figure S2 Three HOMO and LUMO, calculated for dye **1** in MeCN.

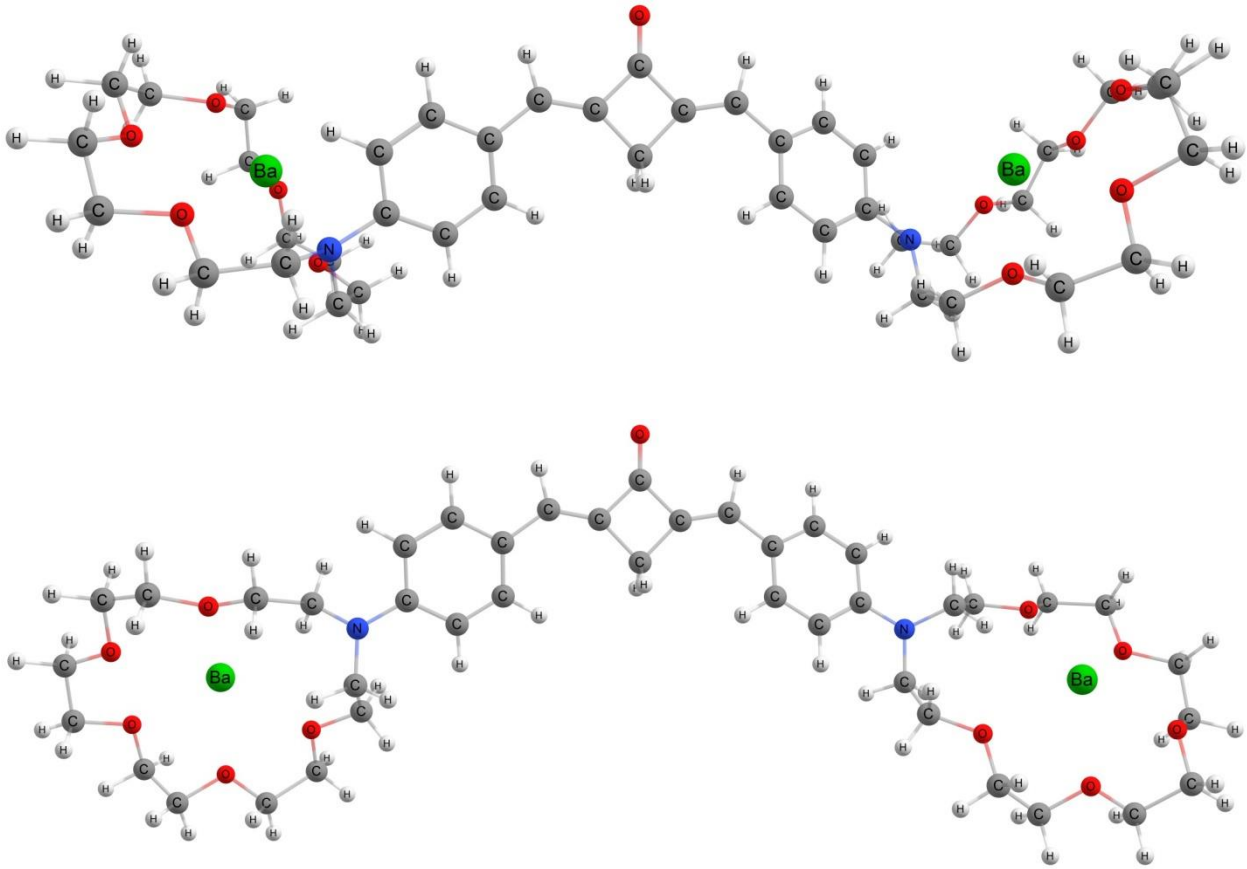


Figure S3 Molecular structure of the complex **1**·$(Ba^{2+})_2$ in axial (up) and equatorial forms (down). Molecules of solvent are not shown.