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Crystal violet's shoulder

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The symmetry of the crystal violet cation has been the subject of ongoing discussion since G. N. Lewis and co-workers called attention to the unexpected shoulder in its optical absorption spectrum. Strikingly absent from this debate is a description of the X-ray crystal structure of the common chloride salt, that compound to which the vast majority of the spectroscopic analyses pertain, and whose large crystals account for the familiar name. This absence is especially curious since a preliminary structure determination was made as early as 1943. Here, we present single crystal structures of two forms of crystal violet chloride, a monoclinic monohydrate and a trigonal nonahydrate. In principle, the pair is well suited to address whether desymmetrization is responsible for the shoulder since the cation is asymmetric in the monoclinic crystal, while it is axially symmetric in the trigonal crystal. Absorption spectra of the two crystalline forms were identical and dominated by peaks assigned to aggregates. Raman spectra also could not distinguish the hydrates from one another. Mixed crystals of benzene-1,2-dicarboxylic acid (phthalic acid) containing mM concentrations of crystal violet were prepared in order to study the cation fixed in a dissymmetric medium, yet free from aggregate absorption. Through this work, and a reevaluation of the literature, we show that the two prevailing theories for the shoulder, that there are two isomers in equilibrium, and that desymmetrization gives rise to two excited states, are not mutually exclusive.

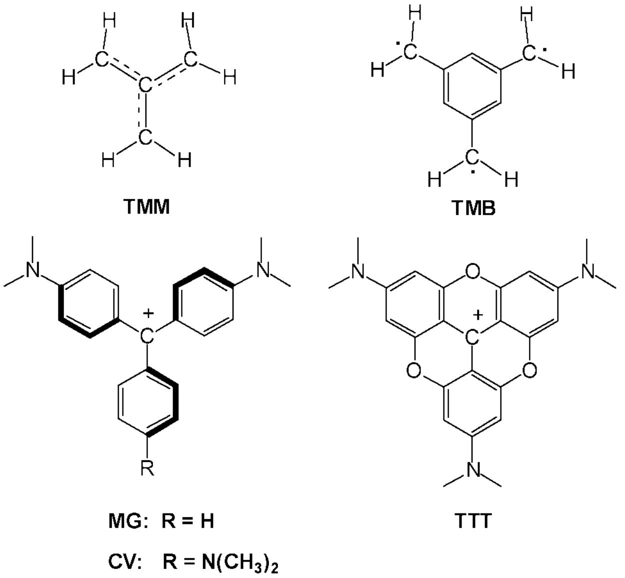
Introduction

In recent years, Robert Squires' trailblazing studies of the electronic structure and gas-phase reactivity of open-shell hydrocarbons forced him to meditate on the symmetry lowering distortions to which such compounds are subject. With Wenthold, Hu, and Lineberger, he showed that the lowest excited singlet state of D_{3h} trimethylenemethane (**TMM**) was the first-order, Jahn–Teller distorted, C_{2v}, A_1 state,[1] a result that mimics the puzzling symmetry lowering in the triplet state of **TMM** first observed by Dowd.[2] With Kemnitz and Borden he showed that 1,3,5-trimethylenebenzene undergoes a similar $D_{3h}\rightarrow C_{2v}$ distortion due to first- as well as second-order Jahn–Teller effects.[3] One of us (BK) did his best to play the role of sounding board as Squires worked through these structural subtleties.

Here, we offer a story about the loss of symmetry in another axially symmetric (D_3) molecule, the dye crystal violet (**CV**, tris(*p*-dimethylaminophenyl)methyl or *N*-(4-{bis[4-(dimethylamino)phenyl]methylene}cyclohexa-2,5-dien-1-ylidene)-*N*-methylmethanaminium chloride, 548-62-9) of which it has been said that as the active ingredient in carbon paper it has stained more hands than any other compound.[4] Ever since Lewis *et al.* (hereafter Lewis) suggested that a troublesome, high-energy shoulder in the electronic absorption spectrum of **CV** was due to a minor conformation of lower symmetry (C_2) with one aryl ring disrotated from the other two[5] (Scheme 1), researchers have returned time and again to speculate on the origin of the misshapen spectrum. We now count ourselves among this group.

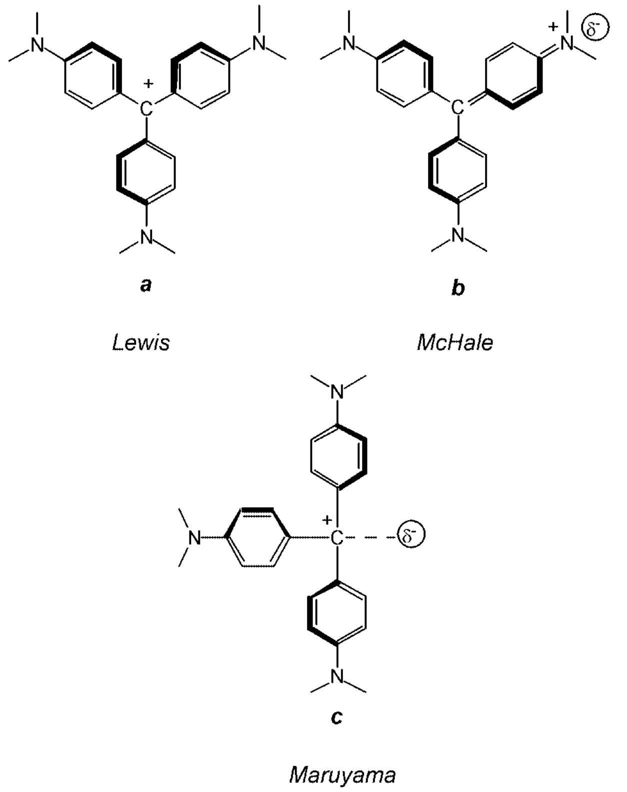
History

Alcohol solutions of **CV** have two optical absorption bands, the characteristic peak (R band) near 600 nm and shoulder (B band) near 550 nm. The B band is diminished with decreasing temperature, suggesting to Lewis an equilibrium process. High-pressure studies were further supportive of an equilibrium between two ground states.[6] However, in light of what we now know about the internal dynamics of triarylmethyl propellers,[7] the distortion envisioned by Lewis (Scheme 2a) can not result in a minimum energy structure. This was demonstrated computationally by McHale and co-workers (hereafter McHale).[8]



Scheme 1

In a scholarly review of the **CV** literature, Maruyama *et al.* (hereafter Maruyama) explained that the Lewis-like proposition of two ground state structures competed with the notion that the two bands arise from transitions to two excited states.[9,10] On the basis of resonance Raman and fluorescence spectroscopies, as well as model INDO/S calculations,[11] McHale argued that dipoles or counter anions (Scheme 2b) interacting with dimethylamino groups of CV^+



Scheme 2

were responsible for lifting the degeneracy of the S_1 E-state, an explanation consistent with the fact that the splitting was greater in non-polar solvents.[5,12,13] Excitation even into the blue edge of the B band gave a fluorescence spectrum that mirrored the R band, a strong indication that the two bands arise from different electronic transitions of a single ground state species. But, since only the Raman depolarization ratios, and not the normal mode assignments, differed from that expected for a D_3-symmetric structure, the authors concluded that the solvent or counterion induced symmetry breaking was "electronic rather than mechanical" in origin.

Korppi-Tommola and co-workers similarly adopted the notion of a split S_1 state.[14,15] They observed temperature dependencies only in alcohols and therefore concluded that the monomer–dimer equilibrium between alcohol molecules precluded the solvent symmetry breaking necessary for the splitting of the S_1 state at low temperatures, where the equilibrium of the solvent molecules favors dimers.

Picosecond pump-probe measurements of the relaxation of the bleached excited state indicated faster recovery on the red side. This observation was attributed to two ground states[16] or to two excited states with different non-radiative decay rates.[17,18] Sundström and Gillbro concluded that either interpretation could be consistent with their data.[16a,b,19]

Most recently, Maruyama showed in the ultra-fast (femtosecond) transient absorption spectra of **CV** in methanol that the temporal rise of the B band was dependent on the excitation wavelength. They concluded that this was the result of an inhomogeneous ground state. In other words, the electronic transitions originate from different species. They proposed yet another structure for the second ground state, a pyramidal C_3-symmetric cation formed by electrostatic interaction with a solvent molecule or counter-ion that pulled the central carbon out of the mean molecular plane (Scheme 2c). Semi-empirical molecular orbital calculations were invoked to bolster this claim.

Two ground states or two excited states? In the face of so much seemingly conflicting evidence, how can we choose? Must we choose?

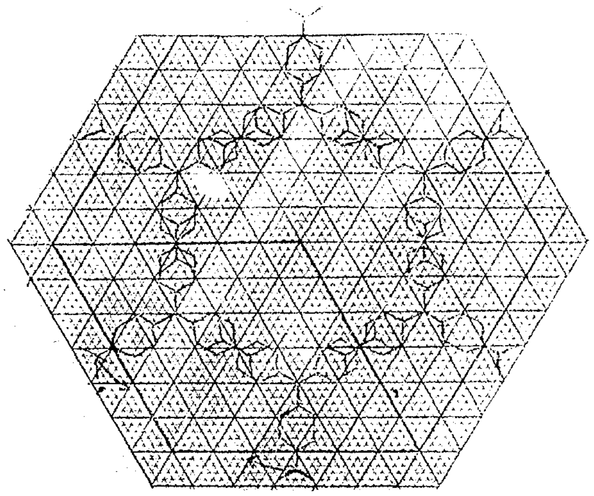


Fig. 1 Krebs's sketch of the trigonal $\mathbf{CV^+Cl^-{\cdot}9H_2O}$ structure from BIOS microfilm. He apologized for his incomplete report that was prepared hastily because he was summoned to the Wehrmacht.[21]

Crystal structures of crystal violet chloride hydrates

All of the above cited studies of **CV** used the chloride salt. An obvious way of evaluating the possibility of structural deviations due to ion–ion pairing in solutions containing **CV** would be to determine the structure of crystal violet chloride ($\mathbf{CV^+Cl^-}$) in the solid state. But, despite the fact that long-standing speculation about the structure and symmetry of **CV** was based upon spectroscopic measurements of its chloride salt, the crystal structure of this compound was never refined. To date, one complete **CV** crystal structure, that of the non-coordinating tetraphenylborate salt can be found in the literature.[20] We report here the crystal structures of two forms of $\mathbf{CV^+Cl^-}$, a trigonal nonahydrate ($\mathbf{CV^+Cl^-{\cdot}9H_2O}$) and a monoclinic monohydrate ($\mathbf{CV^+Cl^-{\cdot}H_2O}$). Each compound contains water molecules and chloride counterions that may well interact with the loci of positive charge (C_{methyl} and N) in **CV**, and thereby break the symmetry in accordance with the respective propositions of McHale and Maruyama.

Nonahydrate ($\mathbf{CV^+Cl^-{\cdot}9H_2O}$)

The determination of the X-ray structure of $\mathbf{CV^+Cl^-}$ was first attempted in 1943 by Krebs, a wartime worker at the I.G. Farben Oppau explosives factory which was eventually bombed by the Allied Forces. On 25 March 1945, British and American investigators organized bands of local Germans to dig through the factory rubble in order to retrieve scientific documents that might aid the Allies in the defeat of Japan. During this search they unearthed a report by Krebs describing his preliminary crystallographic studies, dated 15 June 1943. It was cataloged with the reports of the British Intelligence Objectives Subcommittee (BIOS),[21] one of several special scientific intelligence units formed to collect technical information of military value from the Germans. BIOS microfilms can be obtained from the US Library of Congress.[22]

Krebs reported the following crystal data: $a = 16.02$ Å, $c = 7.86$ Å, space groups $P31c$ (no. 159) or $P\bar{3}1c$ (no. 163), $Z = 2$. In $P31c$ the site symmetry would be C_3, compatible with what we understand today about the symmetry of triarylmethyl cations. The choices in the centrosymmetric supergroup are S_6 and D_3. While the propellers may have D_3 symmetry, the impossibility of an inversion center precludes S_6. In either space group, Krebs required layers of cationic **CV** molecules separated by 3.9 Å. His sketch of this structure is shown in Fig. 1.

Stora returned to $\mathbf{CV^+Cl^-{\cdot}9H_2O}$ in 1949.[23] Her preliminary photographs compare favorably with Krebs's. She surmised

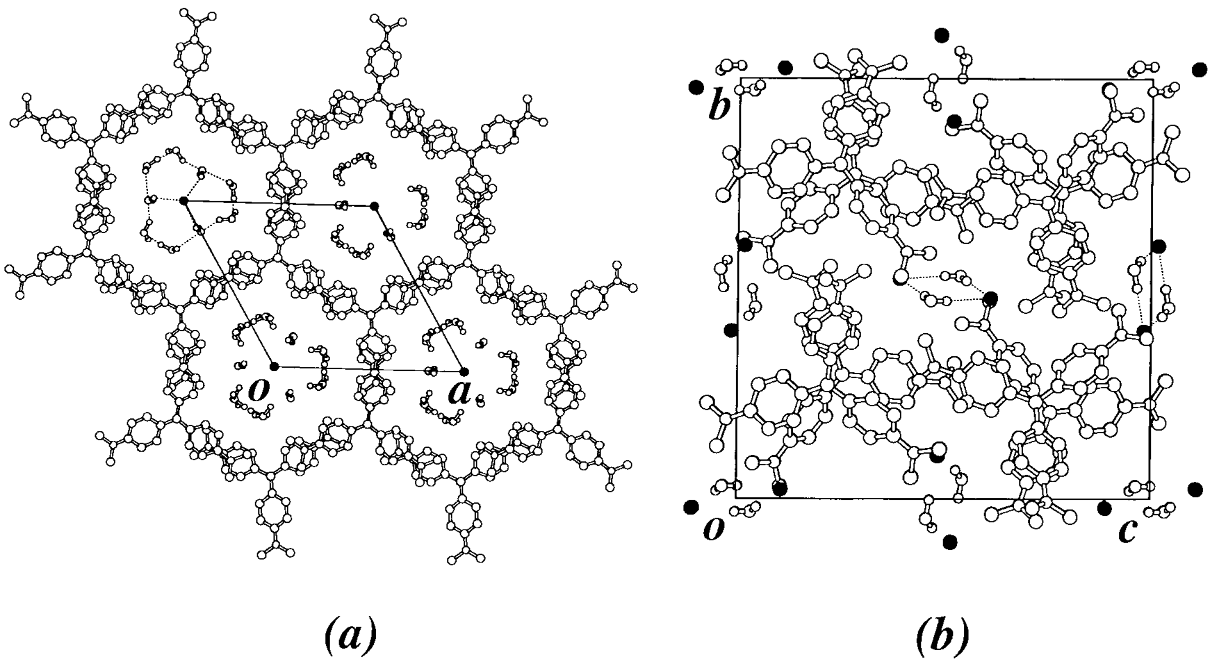


Fig. 2 Crystal packing of (a) the nonahydrate and (b) the monohydrate of $\mathbf{CV^+Cl^-}$. The black circles represent Cl^-. Only water Hs are shown. The H-bonds in half a unit cell are indicated in the upper left channel with dotted lines.

Table 1 Crystallographic data for crystal violet chloride

	$\mathbf{CV^+Cl^-{\cdot}9H_2O}$	$\mathbf{CV^+Cl^-{\cdot}H_2O}$
Formula	$C_{25}H_{30}N_3Cl{\cdot}9H_2O$	$C_{25}H_{30}N_3Cl{\cdot}H_2O$
Molecular weight/g mol^{-1}	570.11	425.99
Crystal system	Trigonal	Monoclinic
Space group	$P31c$ (No. 159)	$P2_1/c$ (No. 14)
Crystal shape/color	Prism/metallic green	Needle/metallic green
Crystal size/mm	0.38 × 0.23 × 0.16	0.31 × 0.08 × 0.08
a/Å	15.7087(4)	10.1877(5)
b/Å	15.7087(4)	21.4842(11)
c/Å	7.4783(2)	21.2594(6)
α/deg.	90	90
β/deg.	90	94.374(3)
γ/deg.	120	90
V/Å^3	1598.14(7)	4640.0(4)
Z	2	8
D_{calc}/g cm^{-1}	1.185	1.220
μ/mm^{-1}	0.169	0.186
T/K	161	161
2θ range/deg	6–58	6–54
Measured reflns.	25709	61131
Independent reflns.	2451	7690
R_{int}	0.031	0.047
No. of data	2451	7690
No. parameters	112	541
GOF	1.067	1.019
R ($F > 4\sigma(F)$)	0.0792	0.0684
wR (all data)	0.2278	0.1933
Largest peak/hole/ e Å^{-3}	0.394/−0.638	0.293/−0.296

that the structure was trigonal, $P31c$ or $P\bar{3}1c$, and concluded that the molecule is "en grande partie plane."[24] We believe that she meant that the ~3.9 Å separating distance precluded pyramidal dye ions and was not a statement about the aryl ring dihedral angles. Stora's work was for many years the only reference to the X-ray structure of **CV** in the open literature. It was interpreted in two ways: some assumed that the molecule was not pyramidal in its coordination about the central carbon, while others inferred that the aryl rings occupied a common plane.

We grew crystals of $\mathbf{CV^+Cl^-{\cdot}9H_2O}$ by cooling a supersaturated water solution. Trigonal prisms ($\{0\,0\,1\}$, $\{0\,0\,\bar{1}\}$, and $\{1\,1\,0\}$) were deposited. Their structure was determined by X-ray crystallography (Table 1). The proper space group for the refined structure was the acentric $P31c$. The absence of the center of symmetry can be detected by inspection (Fig. 2a). The cations are arranged with overlapping dimethylamino groups and form channels along the c-axis that encapsulate water molecules and chloride ions. This channel arrangement resembles the structure in the unpublished sketch by Krebs (Fig. 1).[20] Within the channels, Cl^- ions are located on threefold axes surrounded by H_2Os ($Cl^- \cdots H = 2.956(2)$ Å). The other two symmetry independent H_2Os are bound to each other and to the H_2O interacting with the Cl^- forming a network composed of pentagonal rings. The $O \cdots O$ contacts with this network are 2.723(5) Å, 2.758(8) Å, and 2.852(7) Å. The remaining H atoms are directed along the channel and are weakly bound to the next cluster ($O \cdots O > 3.0$ Å).

There are no close contacts between the C^+ or N loci of the positive charge, and chloride ions or water oxygen atoms. The nearest $C^+ \cdots Cl^-$, $C^+ \cdots O$, $N \cdots Cl^-$, and $N \cdots O$ distances are 9.221(5) Å, 5.378(5) Å, 7.531(6) Å, and 4.743(5) Å, respectively, each well beyond the sums of the van der Waals radii.

The cation has a typical propeller geometry. The dihedral angle between the aryl rings and the central coordination plane is 27.7(1)°. The **CV** ions have local C_3 symmetry and are therefore not crystallographically planar in the coordination of the central carbon atom, however, C^+ rises less than 0.001 Å from the plane defined by the carbon atoms to which it is bonded; the sum of the $C\text{–}C^+\text{–}C$ angles is 360.0(3)°.

Monohydrate ($\mathbf{CV^+Cl^-{\cdot}H_2O}$)[25]

Crystals of the monohydrate were grown by vapor diffusion of ether into acetone. There are heterochiral, asymmetric molecules in the asymmetric unit of a monoclinic $P2_1/c$ cell. The chloride ions and water molecules form hydrogen bonds producing two sets of 8–membered centrosymmetric rings, including Hs (Fig. 2b). Using the Cambridge Structural Database (CSD) Pathaneni *et al.* found that for comparably H-bound cyclic tetrads composed of two H_2Os and 2 Cl^- ions, average $O \cdots Cl$, $Cl \cdots Cl$, and $O \cdots O$ contacts are 3.2(2) Å, 5.0(2) Å, and 3.7(1) Å, respectively.[26] In $\mathbf{CV^+Cl^-{\cdot}H_2O}$ the average $O \cdots Cl$ and $Cl \cdots Cl$ distances are similar ($O \cdots Cl = 3.239(4)$

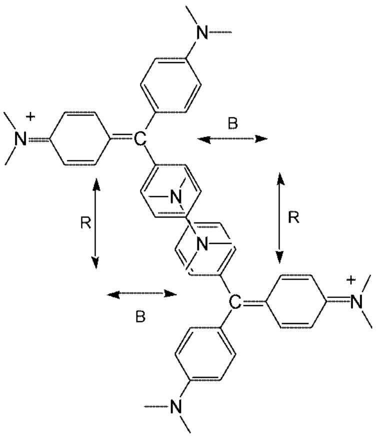
Å, Cl · · · Cl = 4.935(2) Å), but the average O · · · O distances are longer (4.191(4) Å).

The ring dihedral angles, a good measure of dissymmetry for triarylmethyl propellers, are 26.8(2)°, 37.3(1)°, 38.4(2)°, and 28.0(2)°, 33.6(2)°, 36.2(2)°, for the two molecules in the asymmetric unit, respectively. Deviations of the central carbon from its coordination planes are 0.003(4) Å and 0.020(4) Å. The sums of the C–C^+–C angles are 359.7(3)° and 359.9(3)°. As with the nonohydrate, there are no close intermolecular contacts involving C^+ or N. The nearest $C^+ \cdots Cl^-$, $C^+ \cdots O$, $N \cdots Cl^-$, $N \cdots O$ are 5.900(4) Å, 5.793(5) Å, 4.457(4) Å, and 4.243(5) Å, respectively.

In summary, given three symmetry independent **CV** cations in two polymorphs, there is no evidence for pyramidalization nor close contacts to Cl^- or H_2O.

Absorption spectroscopy of single crystals

The absorption spectra of **$CV^+Cl^-·9H_2O$** and **$CV^+Cl^-·H_2O$** were determined with a microabsorption spectrophotometer. In lieu of preferable specular reflection spectra, single crystals were placed on a microscope slide and sandwiched between a second slide that was rubbed across the first producing a translucent lavender film; the spectra were measured immediately thereafter. Both crystalline forms gave a prominent band at 543 nm and a shoulder near 620 nm, the inverse of the relative intensities in a dilute solution. Stork *et al.*[27] investigated the association of **CV** in aqueous solution and showed that at high dye concentrations (>10^{-4} M) a peak at 541 nm increases at the expense of the R band. These results were later confirmed by Lueck *et al.*[28] who explained the observed dimeric bands on the basis of exciton coupling of R and B band transition dipoles as shown in Scheme 3. They proposed a dimer structure in which dimethylamino groups overlap in a head-to-tail manner which maximizes hydrophobic interactions, the driving force for dimerization. This is indeed the pair-wise arrangement of the cations in the crystal structures of **$CV^+Cl^-·9H_2O$** and **$CV^+Cl^-·H_2O$** (Fig. 2).



Scheme 3

Raman spectroscopy

Vibrational spectra of **$CV^+Cl^-·9H_2O$** and **$CV^+Cl^-·H_2O$** were obtained with a micro-Raman spectrometer. A 785 nm laser was focussed below the surface of the crystals so as to avoid artifacts due to dehydration. Despite the fact that we know from the X-ray structure determinations that the ions in the crystals are axially symmetric and asymmetric, the spectra in Fig. 3 and data in Table 2 do not discriminate between the two crystalline forms. Moreover, they are completely consistent with what has been reported previously for dilute solutions.[29] There is a one-to-one correspondence between the peaks of the two hydrates and the peaks for **CV** in solution. Thus, the deviation from axial symmetry for **CV** in the monohydrate is not manifest in the Raman spectra. This is consistent with the analysis of McHale who showed that assignments of the normal modes in solution are more consistent with D_3 than with C_2 symmetry.

Table 2 Raman frequencies (cm^{-1}) for crystal violet chloride

$CV^+Cl^-·9H_2O$	$CV^+Cl^-·H_2O$	Aq. Soln.[29]
212	210	208
343	341	340
428	428	424
447	446	442
531	527	528
565	565	562
609	608	610
729	729	727
748	748	749
764	763	770
808	806	812
918	918	917
945	945	944
984	984	982
996	999	996
1138	1134	1136
1178	1178	1178
1306	1300	1303
1341	1341	1344
1370	1365	1372
1395	1395	1393
1448	1447	1450
1474	1475	1486
1545	1538	1544
1586	1585	1591
1622	1622	1622

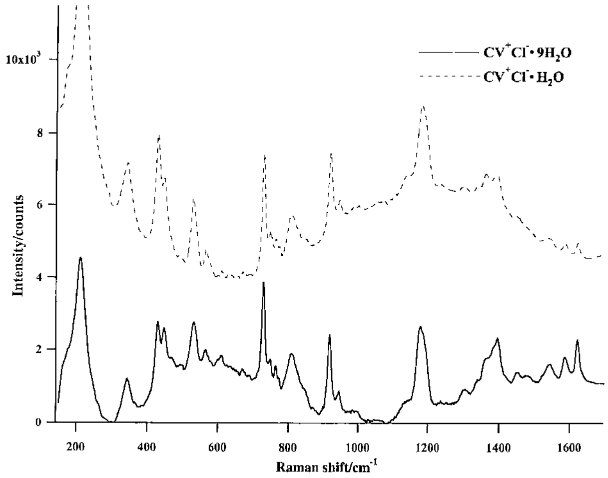


Fig. 3 Raman spectra of **$CV^+Cl^-·9H_2O$** and **$CV^+Cl^-·H_2O$**.

Only the observation of dissymmetry is informative. It is obvious but not always appreciated that one cannot deduce from the absence of any measurable reduction of symmetry that a substance under investigation is symmetric.[30] A compelling example is that here different symmetries in **$CV^+Cl^-·9H_2O$** and **$CV^+Cl^-·H_2O$** give the same Raman spectra to one another and to **CV** in solution.

Mixed crystals

In the context of our general studies of the process of dyeing crystals,[31] we have shown that a variety of aromatic carboxylic acids have a propensity to orient and overgrow cationic dyes in specific growth sectors. We previously grew crystals of phthalic

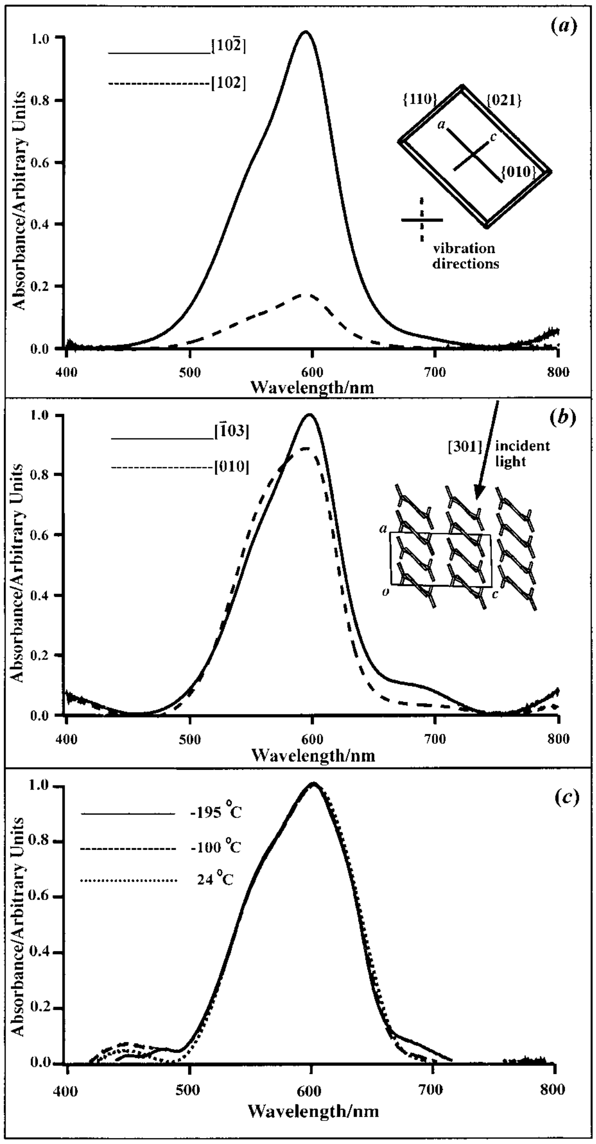


Fig. 4 Absorption spectra of **CV** in phthalic acid. (a) Room temperature spectra for light polarized in the (0 1 0) face; (b) Room temperature spectra for light polarized in the (3 0 1) face; (c) Unpolarized spectra at various temperatures.

acid containing 1 mol **CV** in 12 000 mol phthalic acid.[32] Plates with well-developed {0 1 0} faces were obtained that showed a purple hourglass pattern of color associated with the {0 2 1} growth sectors. The crystals showed strong linear dichroism for light incident upon (0 1 0) with the maximum absorbance observed when the electric vector of the light was linearly polarized along [1 0 $\bar{2}$] (Fig. 4a). The dichroic ratio was 5.8. Both the R and B bands had the same polarization. This is consistent with the model that we had built previously for cationic dyes in phthalic acid crystals in which the mean plane of the aromatic chromophores was parallel to (102). However, for light incident upon the {3 0 1} cleavage planes of phthalic acid we see different polarizations for the R and B bands (Fig. 4b). The B band has gained relative intensity at the expense of the R band. This is suggestive of the fact that in the asymmetric environment of phthalic acid, **CV** loses its degeneracy. With light incident upon the edge of the propeller, all π–π* transitions must have the same polarization, however for light incident upon the face of the propeller, the non-degenerate x and y polarized transitions respond independently.

We next recorded the absorption spectra at low temperature (−195 °C) by mounting a mixed crystal in a Joule–Thomson refrigerator equipped with quartz windows for optical spectroscopy. Under these circumstances, we did not see a change in the relative intensities of the R and B bands, as is observed in solution (Fig. 4c). Here is rather definite evidence that **CV** can show non-axial symmetry in its optical spectra. The shoulder need not be ascribed to an equilibrium between isomers.

Discussion

Raman spectroscopy is not sensitive to small X-ray structural differences between the **CV** hydrates, thus for good reason have past vibrational spectroscopists been unable to pin down the origin of the **CV** shoulder. Moreover, the crystal structures do not inform the mystery surrounding the shoulder, nor do they suggest just what ion–ion, or ion–dipole pairs might exist in solution as the water molecules and chloride ions show a greater affinity for one another than for **CV**. However, from the polarization and temperature dependencies, we can conclude that in a phthalic acid single crystal the symmetry of **CV** has been reduced. Here, we find evidence for two excited states in an environment in which a dynamic equilibrium between two ground states is most likely obviated.

As laid out by Maruyama, the main competing theories of the **CV** shoulder, that ion–ion or ion–dipole pairing leads to a splitting of the S_1 excited state of a single ground state or that two ground states, associated and unassociated, exist at room temperature in equilibrium, are not mutually exclusive. Why must it be one or the other? The ion–ion or ion–dipole pairing by its very nature is an equilibrium process. Thus, the solvent or counter-ion symmetry breaking model of McHale illustrated in Scheme 2b *requires both an equilibrium between two ground states, one of which is non-axial and must have a non-degenerate* S_1 *state.*

If the **CV** spectrum with shoulder actually arises from one D_3 cation peak superimposed on the spectrum of a less symmetric ion with a split S_1 state, then all of the observations of previous researchers would be expected and contradictions would disappear. Maruyama would have observed different recovery times. McHale would have observed luminescence from the R band irrespective of the excitation energy.

Ben-Amotz and Harris have concluded from their picosecond pump-probe experiments that one equilibrium conformation and one electronic excited state dominate the dynamics. However, they concede that their observation of a slightly shorter decay on the blue side of the absorption band can not be discounted as a manifestation of a second ground or excited state.[18]

Maruyama avoided mixing the two competing theories by choosing two ground states, planar and pyramidal, that have threefold, or pseudo-threefold symmetry, respectively. But, while the elegant pump-probe experiments provide strong evidence for two ground states, there is no evidence that one of the ground states is pyramidal.

A search of the Cambridge Structural Database (Version 2.3.7) uncovered 19 triarylmethyl cation X-ray structure determinations. The sum of the C–C$^+$–C angles was in no case less than 359.8° for TADXOL.[33] Excepting this structure, all other C–C$^+$–C angle sums were between 359.9–360°. We have observed that even when the helicity of a triarylmethyl cation is grossly perturbed such as for **MG**$^+$(hydrogen phthalate)$^-$, the ion remains planar about its central atom (NACWOD).[32]

In modeling the solvent induced symmetry lowering transition from D_3 to C_3 using semi-empirical molecular orbital calculations, Maruyama fixed an ethanol oxygen atom 2 Å from the positively charged C_{methyl} carbon, too long for a C–O bond, and much shorter than a non-bonded interaction. Naturally, at this distance there will be a great tendency toward a C_{methyl} tetrahedral coordination geometry. The recently synthesized 2,6,10-tris(diethylamino)-4,8,12-trioxatriangulenium planar cation (**TTT**) displays precisely the same bandshape as **CV** with a peak at 471 nm and a shoulder near 450 nm in dichloromethane.[34] It would be even more difficult in this case to rationalize the shoulder in terms of a pyramidal distortion given the three oxo-bridges.

The second species of the equilibrium first postulated by Lewis and confirmed by Maruyama using ultra-fast spectroscopy cannot be due to cation pyramidalization. The proposed structure of McHale in which a cation or solvent molecule is coordinated to a nitrogen atom, is certainly a possible candidate. We have shown that **MG** in an asymmetric environment can undergo considerable distortion due to the formation of a charge transfer complex with a hydrogen phthalate anion. The existence of such a species implies that in solution there must be two minima on the ground state surface, the dissymmetric complex with two excited states, as well as the cation that presumably preserves the full symmetry in solution. Given the temperature dependencies of the **CV** bands observed by Lewis, the two purported ground state species must be nearly equi-energetic ($\Delta G < 1$ kcal mol^{-1}); it is likely they are both significant in solution at room temperature. The seemingly contradictory data support the notion that there are two ground states *and* two excited states.

Experimental

X-Ray crystal structure determinations

Samples for X-ray analysis were mounted on glass capillaries in epoxy. Diffraction data were collected with a Nonius KappaCCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Data were collected with ω-scans in 1° increments over 180°. For **$CV^+Cl^-\cdot H_2O$** we used 15 s exposures per frame whereas for **$CV^+Cl^-\cdot 9H_2O$** we used 60 s exposures. Crystal-to-detector distance was 28 mm. All hydrogen atoms were located by difference Fourier synthesis and refined with a riding model. U_{iso} for H atoms were fixed such that they were 1.1 (C*H*) or 1.5 (O*H*) times U_{iso} of their parent atom. Integration of intensities and unit cell refinement were performed with the DENZO-SMN[35] package. Structure solution was carried out using the direct methods program SIR92[36] and refined using SHELXL-97.[37] Data were not corrected for absorption.†

Mixed crystal growth

A saturated aqueous solution of phthalic acid was heated to approximately 75 °C. One mL of the hot solution was placed on a microscope slide and 2–4 drops of **CV** (~10^{-3} M) in distilled water was added. The solution was cooled to room temperature. After approximately 15 minutes {0 1 0} plates formed. The slide was then washed with hexanes to remove water and prevent etching. Crystals were cleaved by applying pressure with a razor blade.

Absorption spectroscopy

Absorption spectra were measured with a SpectraCode Multipoint-Absorbance-Imaging (MAI-20) Microscope which consists of an Olympus BX-50 polarizing microscope connected to a Spectra Pro-300i triple grating monochromator (Acton Research Corporation). An optical cable containing a linear stack of 20 fibers connects the microscope to the monochromator coupled to a Princeton Instruments CCD detector. The instrument is controlled with a Macintosh IIfx computer using the program KestrelSpec. Crystals were aligned at an extinction position and spectra were measured for orthogonal polarizations directions. Corrections of the absorbance for birefringence[38,39] were not applied as they were well within the errors in crystal position. Low sample temperatures were achieved with an MMR Technologies 377-0 Joule–Thomson refrigerator.

Raman spectroscopy

Spectra were collected with a Kaiser Optical Systems Hololab Series 5000 Raman microscope consisting of a Holoprobe transmission holographic spectrograph interfaced to the infinity-corrected, fiber-coupled Olympus microscope. The Raman spectra were measured using a thermoelectrically cooled CCD. A beam splitter between the fiber-optic probe head and the microscope provided a real-time visual channel for the simultaneous full-color display of the sample image and the laser spot on the sample. The microscope used in this study was configured with a single mode excitation fiber and a multimode collection fiber. A 20 ×, 0.25 numerical aperture microscope objective lens provided a confocal 5.5 µm diameter spot at the sample. The optical power at the sample was approximately 50 mW. The Holoprobe was configured with a 785 nm stabilized external cavity diode laser and a split configuration Holoplex transmission grating for simultaneous collection of the high (1600 cm^{-1}) and low (200 cm^{-1}) frequency Raman spectra. Data were acquired using a 50 µm slit width and a detector temperature of −40 °C. The spectra were the average of 5 accumulations of 5 s exposures.

Acknowledgements

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References

1 P. G. Wenthold, J. Hu, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1996, **118**, 475.
2 P. Dowd and M. Chow, *J. Am. Chem. Soc.*, 1977, **99**, 2825.
3 C. R. Kemnitz, R. R. Squires and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 6564.
4 P. J. Wingate, *The Colorful DuPont Company*, Serendipity Press, Wilmington, Delaware, 1982.
5 G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, 1942, **64**, 1774.
6 F. T. Clark and H. G. Drickamer, *J. Chem. Phys.*, 1984, **81**, 3463; F. T. Clark and H. G. Drickamer, *J. Phys. Chem.*, 1986, **90**, 589.
7 K. Mislow, D. Gust, P. Finocchiaro and R. J. Boettcher, *Fortschr. Chem. Forsch.*, 1974, **47**, 1; K. Mislow, *Acc. Chem. Res.*, 1976, **9**, 26.
8 H. B. Lueck, J. L. McHale and W. D. Edwards, *J. Am. Chem. Soc.*, 1992, **114**, 2342.
9 Y. Maruyama, M. Ishikawa and H. Satozono, *J. Am. Chem. Soc.*, 1996, **118**, 6257. See also: M. Ishikawa and Y. Maruyama, *Chem. Phys. Lett.*, 1994, **219**, 416.
10 A proposed resolution of vibronic structure is unlikely given the independent temperature and pressure dependencies of the two bands. See: L. Angeloni, G. Smulevich and M. P. Marzocchi, *J. Mol. Struct.*, 1980, **61**, 331.
11 J. Ridley and M. C. Zerner, *Theor. Chim. Acta*, 1973, **32**, 111; 1976, **42**, 223.
12 The ion pair hypothesis was recently supported by García-Río who showed that perchlorate, but not chloride, inhibited the de-coloration of **CV** solutions with hydroxide. However, their interpretation is based on the long discredited dual propeller model of Lewis. See: L. García-Río, P. Hervés, J. R. Leis and J. C. Mejuto, *J. Chem. Res.*, (*S*), 1997, 326.
13 Adam and Simpson already surmised that $CV^+ClO_4^-$ forms a tight ion pair. See: F. C. Adam and W. T. Simpson, *J. Mol. Spectrosc.*, 1959, **3**, 363.
14 J. Korppi-Tommola and R. W. Yip, *Can. J. Chem.*, 1981, **59**, 191.
15 Although a later paper by the same authors contradicts the first. Here, the two electronic state model is preferred. See: J. Korppi-Tommola, E. Kolehmainen and E. Salo, *Chem. Phys. Lett.*, 1984, **104**, 373.

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† CCDC reference number 188/185. See http://www.rsc.org/suppdata/p2/1999/2241 for crystallographic files in .cif format.

16 V. Sundström and T. Gillbro, *J. Chem. Phys.*, 1984, **81**, 3463; V. Sundström, T. Gillbro and H. Bergstrom, *Chem. Phys.*, 1982, **73**, 439; J. M. Grzybowski, S. E. Sugmori, D. F. Williams and R. W. Yip, *Chem. Phys. Lett.*, 1979, **65**, 456.

17 R. Menzel, C. W. Hoganson and M. W. Windsor, *Chem. Phys. Lett.*, 1985, **120**, 29.

18 Ben-Amotz and Harris invoked stimulated emission to account for the relaxation dynamics, thereby obviating the need to multiply ground or excited states. See: D. Ben-Amotz and C. B. Harris, *Chem. Phys. Lett.*, 1985, **119**, 305; *J. Chem. Phys.*, 1987, **86**, 4856. For two years from 1990–92 Ben-Amotz, Squires and BK shared a suite of laboratories. This time was among the most stimulating period of the author's professional life. See: L. S. Sunderlin, J. A. Paulino, J. Chow, B. Kahr, D. Ben-Amotz and R. R. Squires, *J. Am. Chem. Soc.*, 1991, **113**, 5489.

19 See also papers on ethyl violet by Martin and co-workers: M. M. Martin, E. Breheret, F. Nesa and Y. H. Meyer, *Chem. Phys.*, 1989, **130**, 279; M. M. Martin, P. Plaza and Y. H. Meyer, *Chem. Phys.*, 1991, **153**, 297; M. M. Martin, P. Plaza and Y. H. Meyer, *J. Phys. Chem.*, 1991, **95**, 9310.

20 B. D. Spangler, P. Vanysek, I. C. Hernandez and R. D. Rogers, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 589.

21 BIOS microfilm, R20, P. B. 73,654, FDX 226.

22 J. Gimbel, *Science, Technology and Reparations. Exploitation and Plunder in Postwar Germany*, Stanford University Press, Standford, 1990; Numerical Index to the Bibliography of Scientific and Industrial Reports, vol 1–10, 1946–48, Edwards Bros, Ann Arbor, Michigan, 1949.

23 C. Stora and G. Eller, *Comp. Rend.*, 1949, **229**, 766.

24 C. Stora, *Comp. Rend.*, 1958, **246**, 1693.

25 A picture from our provisional structure determination of the monohydrate appeared previously. See: B. Kahr and M. P. Kelley, in *Supramolecular Stereochemistry*, NATO ASI Series C: Mathematical and Physical Sciences, vol. 473, (J. S. Siegel, ed.) Kluwer Academic Publishers, Netherlands, 1995, p. 203.

26 S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc.*, *Dalton Trans.*, **1993**, 2505.

27 W. H. J. Stork, G. J. M. Lippits and M. Mandel, *J. Phys. Chem.*, 1972, **76**, 1772.

28 H. B. Lueck, B. L. Rice and J. L. McHale, *Spectrochim. Acta*, *Part A*, 1992, **48**, 819.

29 H. B. Lueck, D. C. Daniel and J. L. McHale, *J. Raman Spectrosc.*, 1993, **24**, 363.

30 K. Mislow and P. Bickart, *Isr. J. Chem.*, 1976/77, **15**, 1.

31 See for example: S.-H. Jang, J. A. Subramony, L. Bastin and M. P. Kelley, *Adv. Mat.*, 1996, **8**, 941; J. A. Chmielewski, J. L. Lewis, S. Lovell, R. Zutshi, P. Savickas, C. A. Mitchell, J. A. Subramony and B. Kahr, *J. Am. Chem. Soc.*, 1997, **119**, 10565; C. A. Mitchell, R. Gurney and B. Kahr, *J. Am. Chem. Soc.*, 1998, **120**, 9726.

32 C. A. Mitchell, S. Lovell, K. Thomas, P. Savickas and B. Kahr, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **35**, 1021. For **CV** in crystals of poppy acid, see: S. Lovell, P. Subramony and B. Kahr, *J. Am. Chem. Soc.*, 1999, **121**, 7020.

33 The relevant refcodes are the following: APCRBP10, HEZBIX, KOHVOS, KUBLUO, MACWOD, PCBTEC10, RINJUT, SAZNOW, TAGSOJ, TEJXOV, TIPMEP, VIGXUE, VIGYAL, VIRDAB, VIRDEF, YEVVOK, ZUWCEZ.

34 B. W. Laursen, F. C. Krebs, M. F. Nielsen, K. Bechgaard, J. B. Christensen and N. Harrit, *J. Am. Chem. Soc.*, 1998, **120**, 12255.

35 Z. Otinowski and W. Minor, *Methods in Enzymology*, C. W. Carter, Jr. and R. M. Sweet, eds. Academic Press, New York, 1996, p. 307.

36 A. Altomare, G. Cascarano, C. Giacovazzo, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

37 G. M. Sheldrick, *SHELXL97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

38 J. Michl and E. W. Thulstrup, *Spectroscopy with Polarized Light*, VCH, New York, 1986.

39 A. N. Winchell, *The Optical Properties of Organic Compounds*, McCrone Research Institute, Chicago, 1987, p. 190.

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