

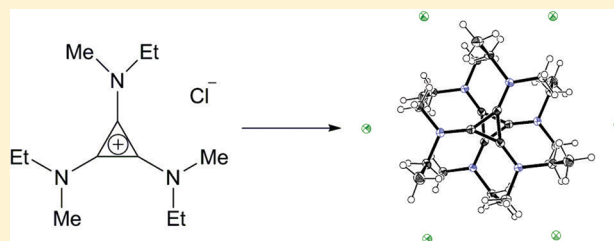
Cyclopropenium Cations Break the Rules of Attraction to Form Closely Bound Dimers

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S Supporting Information

ABSTRACT: The crystal structures of tris(ethylmethylamino)-cyclopropenium chloride and tris(diethylamino)-cyclopropenium iodide reveal the presence of closely bound dicationic dimers formed from two closed-shell monomer units. The distances between the C_3 centroids of the staggered monomers are at the short end of those normally found in π -stacked neutral arenes, let alone charged aromatic rings. Computational analysis reveals that short-range interactions are dominated by strong dispersion forces, enabling metastable dicationic dimers to form without covalent intermolecular bonding. Surrounding counterions then provide a background source of charge balance, imparting strong thermodynamic stability to the system. Additionally, these counterions form a weak but attractive electrostatic bridge between the monomer units, contributing to the surprisingly short observed intermolecular C_3 – C_3 centroid distance.



INTRODUCTION

Ionic liquids (ILs) are chemically interesting materials that are finding increasing practical applications due to their useful physical properties such as negligible volatility, good conductivity, and an ability to dissolve a wide range of solutes.¹ These properties arise from the unusual chemical environment created by a mixture of ions in the liquid state; although ILs often consist of weakly polar molecules, they usually behave like polar solvents. However, they can also exhibit nonhomogeneous behavior, with both hydrophilic (ion-rich) and hydrophobic (alkyl-rich) regions in a dynamic equilibrium.^{2–6} Understanding the balance of intermolecular interactions within ILs that determine ion mobility, ion pairing and ion clustering, and their effects on the properties of ILs, is a fundamental problem of continuing interest.

We recently described the use of triaminocyclopropenium (TAC) cations, $[C_3(NR_2)_3]^+$, in ionic liquids.⁷ These cations are geometrically and electronically quite different from other aromatic cations commonly used for ionic liquids, such as imidazolium and pyridinium, exhibiting higher symmetry with a three-membered all-carbon aromatic ring, and electron-donating amino substituents rather than N atoms incorporated into the aromatic ring. A high-lying HOMO also results in an unusually low and reversible oxidation potential.^{8,9} Consequently, TAC salts have attracted much interest^{10,11} since they were first reported in 1971 by Yoshida and Tawara.¹²

TAC cations also demonstrate unusually weak short-range electrostatic interactions with surrounding counterions. This is manifest in the observation that halide counterions eschew interactions with the TAC cation, preferentially coordinating to other compounds instead. For example, Weiss has commented that “[t]ypically enough, the halides cannot be obtained in

solvent-free form”.¹³ Chloride hydrates,^{14,15} iodide-iodoacetylene,¹⁶ and iodide-iodoarene¹⁷ adducts have all been isolated from tris(dialkylamino)-cyclopropenium (TDAC) halide salts. In particular, the dichloride hexahydrate structure shows essentially no distortion from its calculated gas phase structure, in contrast to those found with other cations.^{14,15}

This apparent preference of TAC cations to coordinate to species other than counterions may even lead to them coordinating to one another to form so-called “ π -dimers” or “ π -stacks”, rather than adopting more conventional intercalated salt structures.

EXPERIMENTAL DETAILS

As part of our ongoing studies on TAC ionic liquids, we have prepared tris(ethylmethylamino)cyclopropenium chloride (**1**) and tris(diethylamino)cyclopropenium iodide (**2**). Salt **1** was prepared by the reaction of C_3Cl_5H with $NEtMeH$, whereas salt **2** was prepared by reaction of $[C_3(NEt_2)_3]Cl$ with EtI . Bielawski has reported similar reactions of halide salts with alkylating agents, such as Me_2SO_4 , $MeOTs$ and $[R_3O]BF_4$;¹⁸ however, we believe this is the first synthesis of an iodide salt by reaction of a chloride with EtI . Ion chromatography confirmed that the chloride had been replaced very efficiently by this route. Single crystals of these materials slowly formed in the neat liquids. Milyukov recently reported the synthesis of **2** via metathesis of the chloride salt with KI .¹⁹ They also reported its room temperature crystal structure.

RESULTS AND DISCUSSION

Crystal Structures. The 120 K P-1 solid state structure of **1** reveals *solvent-free* close-packed layers of triaminocycloprope-

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nium dimers with chloride anions at the hexagonal vertices within the layers (Figure 1a). The most noteworthy aspect of

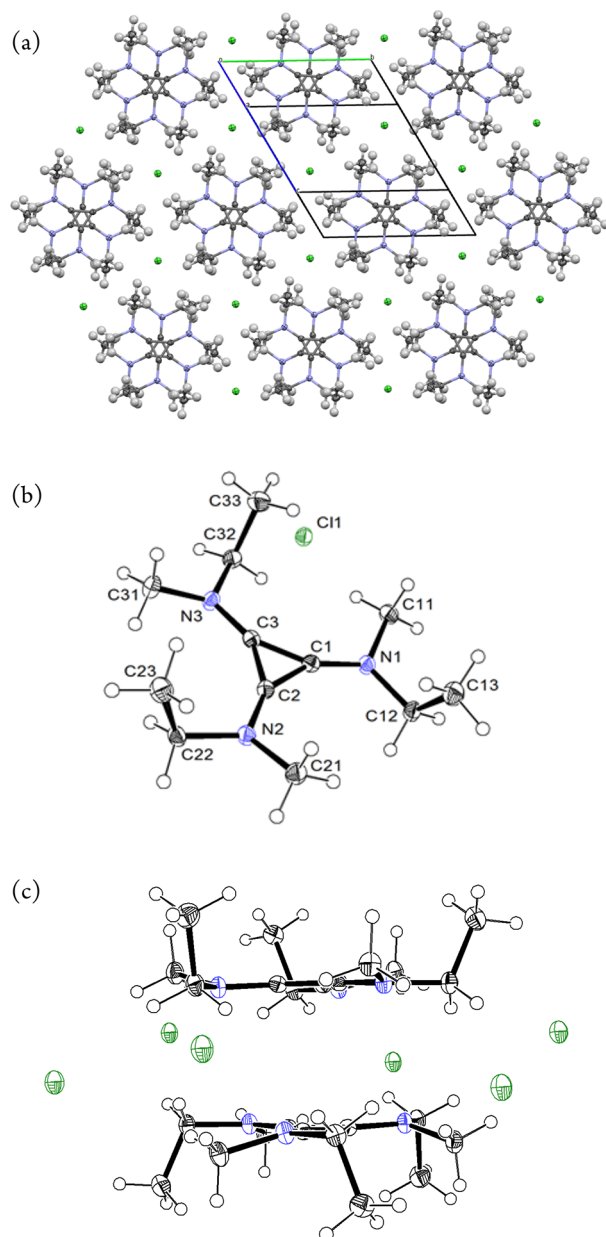


Figure 1. (a) Hexagonal layering of **1**. (b) Cation of **1** with the atomic numbering scheme. (c) Side-on view of the dicationic dimer unit with surrounding counterions. Atoms are represented as 40% probability thermal ellipsoids.

the structure is the short distance between the cations (Figure 1c), with the cyclopropenium C_3 centroids separated by only 3.2251(13) Å. This means the two positively charged aromatics are closer than in most “ π -stacked” neutral arenes at 3.3–3.8 Å.^{20–25} The interlayer distance in graphite, to give another useful comparison, is 3.35 Å.

It is also worth noting that the anions appear to be associated with the alkyl CH groups rather than the formally cationic C_3N_3 core, although this is not without precedent in the literature. The solid state structure of unsolvated $[C_3(NC_y)_2(NEt_2)]Cl$ was recently reported, also with Cl^-

ions in close proximity to the alkyl groups.²⁶ In this case, it appears the bulky amino groups prevent dimer formation.

The view down the intermolecular C_3-C_3 centroid–centroid axis indicates that each Me group lies over an Et group. Steric repulsion between the protons on these groups appears to push the Me groups out of the plane more than the bulkier Et groups which would be interacting more with the layers above and below.

The 120 K solid state structure of **2** was also determined to explore the effect of changing alkyl substituents and counterions (Figure 2). The low temperature $[C_3(NEt_2)_3]I$ structure

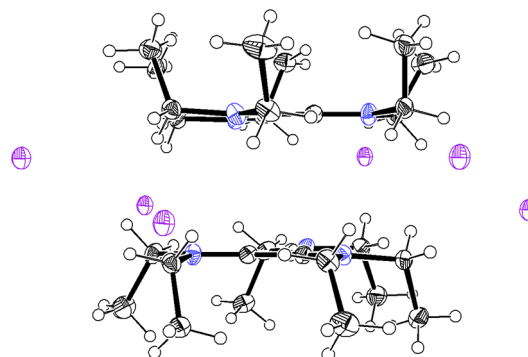


Figure 2. Side-on view of the dicationic dimer unit with surrounding counterions for compound **2**. Atoms are represented as 40% probability thermal ellipsoids.

was solved in the same space group as the previous room temperature structure¹⁹ ($C_{2/c}$) with two cation/anion pairs per unit cell. Despite the different space groups of **1** and **2**, the packing is quite similar to the chloride salt described above, with the extended structure also consisting of TAC sandwich dimers in a close-packed layer arrangement with the iodide anions within these layers. Again, the dimers are in a staggered conformation, and in close proximity to one another with a C_3-C_3 distance of 3.351(2) Å.

A detailed side-by-side comparison of structural parameters for compounds **1** and **2** is presented in Table 1. These observations raise some interesting questions: Why does the dicationic dimer form in preference to more conventional structures with alternating cations and anions? Why is the intermonomer distance so short? What are the fundamental interactions responsible for stabilizing the dicationic sandwich motif?

Computational Analysis. To address these questions, interaction energy curves were calculated for the dissociating dimer of compound **1** as an isolated system in the gas phase, and with the crystalline environment modeled using explicit chloride counterions with a partial nuclear charge model used to ensure overall charge balance while maintaining point-group symmetry in the system ($Z_{\text{eff}} = 17.666$). The three closest counterions were assigned to each monomer unit (Figure 1c) and displaced accordingly upon dissociation. Gas phase potential energy curves were evaluated at MP2/jun-cc-pVDZ and SAPT0/jun-cc-pVDZ while counterion charge-balanced energies were evaluated at MP2/jun-cc-pVDZ only. MP2 energies were corrected for basis set superposition error throughout. Local well depths for metastable complexes were recalculated at SAPT0/aug-cc-pVDZ and SAPT0/jun-cc-pVTZ. Further details of the computational methods and references are available in the Supporting Information. All interaction

Table 1. Observations on the Crystal Structures of 1 and 2

Parameter ^a	1	2	Observation/Comment
$r_{C_3-C_3}$	3.2251(13) Å	3.351(2) Å	remarkably short relative even to neutral π -stacked dimers
$r_{N_3-N_3}$	3.1195(13) Å	3.287(2) Å	nitrogen atoms bent slightly toward center of dimer
$r_{Me_3-Me_3}$	3.8356(13) Å	–	methyl groups bent significantly away from center of dimer 1
$\varphi_{C-C-N,Me}$	21.9°	–	
$r_{Et_3-Et_3}$	3.1099(13) Å	3.4380(18) Å	ethyl groups bend either slightly toward the center of the dimer 1 or slightly away from the center of the dimer 2
$\varphi_{C-C-N,Et}$	–4.9°	6.6°	
r_{C-C}	1.384(2) Å	1.383(3) Å	relatively short C–C distances reflect aromatic nature of TAC ⁺
r_{C-N}	1.329(4) Å	1.330(5) Å	relatively short C–N distances confirm delocalized aromatic system extends out to N atoms
$\{r_{Cl-Me}, r_{Cl-Et}, r_{Cl-Et\beta}\}$	3.56–4.31 Å	3.94–4.53 Å	relatively long halide–ethyl/methyl carbon distances indicate only weak long-range electrostatic interactions may be present

^aC denotes the cyclopropenium carbons, Me denotes the methyl carbons, Et denotes the methylene carbons of the ethyl substituent, Et β denotes the terminal carbons of the ethyl substituent. The 3 subscript denotes the corresponding centroid of all symmetry equivalent atoms within the molecule.

energies are reported relative to the infinitely separated monomer units, and all displacements relative to the experimental intermolecular C_3-C_3 centroid distance for 1.

To investigate the energetics of dicationic dimer formation, it is necessary to initially exclude long-range electrostatic stabilization effects. Therefore, isolated dimer interaction energy curves are presented in Figure 3.

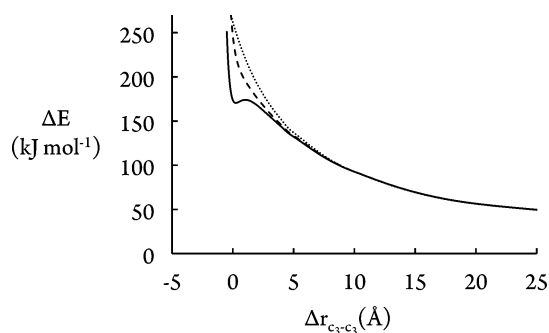


Figure 3. BSSE-corrected HF/jun-cc-pVDZ (dashed line), SAPTO/jun-cc-pVDZ and MP2/jun-cc-pVDZ (solid line, indistinguishable) interaction energy curves, and extrapolated $1/r$ asymptotic electrostatic potential energy curve (dotted line).

These interaction energy curves reveal that intermolecular electron correlation, i.e. dispersion, is the primary force driving dimerization at short-range. Only methods that account for intermonomer electron correlation predict transient metastable complex formation, which can then be “locked in” by long-range electrostatic interactions with the surrounding crystalline matrix. Conversely, if dispersion forces were unable to overcome the “baseline” electrostatic repulsion to create a metastable dicationic dimer complex, then this motif would not occur within the crystalline environment at all; that is, some other packing arrangement would be observed.

It is widely acknowledged that modeling crystal packing forces and predicting solid state structures from gas phase interaction potentials is a complex and challenging problem.²⁷ However, all modern approaches to solving this problem agree that proximal environmental effects are best captured using screened or fuzzy charge models,^{28–32} while longer range electrostatic interactions can be well described using classical point charge or polarizable dipole models.³²

In this spirit, we employ six chloride counterions with fictitious nuclear charges of 17.666 such that each counterion overall carries a partial negative charge of 0.333, as the simplest

possible approach that is consistent with obtaining the correct asymptotic electrostatic behavior of the surrounding environment while maintaining a realistic density-based representation of the counterions closest to each dicationic dimer unit.

Interaction energy curves for the dissociation of this “charge balanced” system along the C_3-C_3 centroid axis are illustrated in Figure 4.

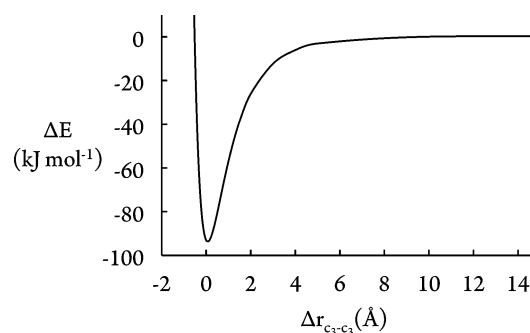


Figure 4. BSSE-corrected MP2/jun-cc-pVDZ interaction potential for dicationic dimer dissociation, with three partially charged Cl^- ions surrounding each monomer unit. The predicted minimum lies within 0.07 Å of the observed C_3-C_3 centroid distance, validating our partial charge model for the crystalline environment.

The stabilization enthalpy of $-93.7 \text{ kJ mol}^{-1}$ can only be considered an extreme lower bound to the experimental enthalpy of formation, given the approximate treatment of environmental interactions. Nonetheless, these results clearly demonstrate the well-known contribution that long-range electrostatic interactions make to the high thermal stability of these compounds.

Closer inspection of Figures 3 and 4 reveals that the position of the metastable local minimum in the gas phase is slightly longer than in the condensed phase, at distances of 3.47 and 3.30 Å, respectively. This difference can be attributed to the chloride counterions forming a weak electrostatic bridge at short-range, in addition to providing long-range electrostatic stabilization. This enhanced interaction between monomer units leads to the remarkably short experimentally observed intermolecular C_3 centroid distance. The iodide ions in complex 2 form a weaker electrostatic bridge, due to their larger ionic radii and lower electronegativities, resulting in the greater experimentally observed intermonomer separation.

Overall, these results are consistent with previous computational studies on dicationic and dianionic dimers formed from

charged organic radical species, which concluded that dispersion was the dominant short-range stabilizing force in these systems, with intermolecular π -bond formation playing a secondary role.^{33–40} For the TAC⁺ dimer, the story is even neater, as the closed-shell nature of the monomer units prohibits intermolecular bond formation, further evidenced by the purely repulsive HF curve and molecular orbital analysis (Supporting Information). Therefore, dispersion forces primarily drive dicationic dimer formation in these systems, while the surrounding counterions form an additional weak electrostatic bridge between the monomer units at short-range, but more importantly provide a long-range background source of charge balance to stabilize each dicationic dimer within the crystalline environment. Without these attractive dispersion interactions between monomer units, crystal packing forces would likely lead to the formation of more conventional structures with alternating cations and anions.

Finally, it remains to consider the electrostatic properties of the monomer units. Existing evidence suggests that the positive charge is delocalized over the TAC scaffold.^{8,9,13–17} Atom-centered density partitioning and electrostatic potential fitting analyses of the HF density (Supporting Information) agree that the positive charge is delocalized over the carbon and hydrogen atoms, while the nitrogen atoms carry partial negative charges. The ethyl and methyl substituents carry a much larger share of the positive unit charge than the inner cyclopropenium ring. This implies that dicationic dimer formation depends on the ability of each monomer to “hide” positive charge away from the dimer interface.

Local well depths for metastable dimers with varying sizes of amino groups are presented in Table 2. Dimer formation becomes more favorable with alkyl substitution and increasing alkyl chain length, as the positive charge becomes increasingly delocalized.

Table 2. Local Well Depths (kJ mol⁻¹) in SAPT0 Dissociation Energy Curves for Gas Phase Dicationic Dimers

amino groups	jun-cc-pVDZ	aug-cc-pVDZ	jun-cc-pVTZ
NEt ₂ (2)	6.7	14.1	14.8
NEtMe (1)	5.3	12.2	12.9
NMe ₂	4.3	11.3	12.1
NH ₂	no local well, repulsive potential		

The 60° rotational offset around the intermonomer axis observed experimentally also serves to minimize the electrostatic repulsion between monomer units and allow transient dimer formation, as illustrated by the aligned and rotationally offset interaction energy curves in Figure 5.

CONCLUSION

In summary, these remarkable systems are paradigm-shifting in a number of ways: they represent the first known example of *unsolvated* TDAC halides, in which the cationic cyclopropenium monomer units preferentially coordinate to one another rather than the surrounding counterions or solvent molecules. Even more remarkably, the monomers are found *closer together than usually observed* in “ π -stacked” systems of neutral aromatics. Counterintuitively, dicationic dimer formation is mainly driven by *strong dispersion interactions* supplemented by *relatively weak electrostatic interactions with counterions at short-range*, and consolidated by long-range electrostatic interactions that charge

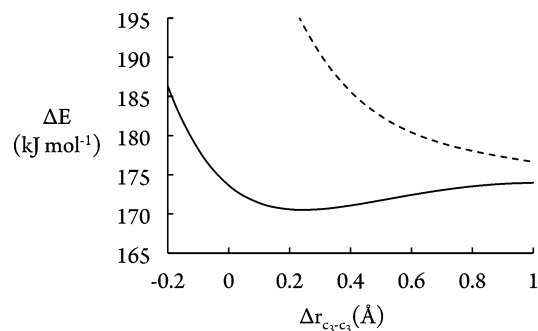


Figure 5. BSSE-corrected MP2/jun-cc-pVDZ interaction energy curves for the aligned dimer 1 (dashed line) and the rotationally offset conformation (the solid line represents a subset of data from Figure 3).

balance the system. This novel observation turns the textbook understanding of intermolecular interactions on its head.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10388. Full crystallographic data is also available from the Cambridge Crystallographic Data Centre (CCDC 1062303 and 1062302).

Full experimental details concerning the synthesis, crystallization, characterization and crystallographic data; computational methods, optimized molecular coordinates of dicationic dimer surrounded by chloride counterions with scaled nuclear charges, and ab initio data including absolute energies in Hartrees underlying all figures, molecular orbital plots, and atomic partial charges (PDF)

Crystallographic data for tris(ethylmethylamino)-cyclopropenium chloride, compound 1 (CIF)

Crystallographic data for tris(diethylamino)-cyclopropenium iodide, compound 2 (CIF)

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Notes

The authors declare no competing financial interest.

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