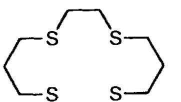
Intramolecular Interactions between Sulfur Atoms in Cyclotetrathioether Radical Cations

Jacek Rogowski,[a] **Jan Adamus,**[a] **Jerzy Gebicki** *,[a] **and Stephen F. Nelsen** *,[b]
[a] *Institute of Applied Radiation Chemistry, Technical University of Lodz, 90-924 Lodz, Poland*
[b] *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA*

Radical cations generated by low temperature steady-state and pulse radiolysis from 1,4,8,11-tetrathiocyclotetradecane (**1**) and derivatives bearing *gem*-dimethyl pairs at the 6- or at the 6- and 13-positions (**2** and **3**, respectively) are characterized by optical absorption spectroscopy. Despite very different conformations for the neutral compounds **1**–**3** their radical cations ($\mathbf{1}^{\cdot +}$–$\mathbf{3}^{\cdot +}$) possess similarly located $\sigma \rightarrow \sigma^*$ transitions (about 450 nm) for structures characterized by the strongest interactions between sulfur atoms. Delayed formation of characteristic absorptions for $\mathbf{2}^{\cdot +}$ and $\mathbf{3}^{\cdot +}$ indicates that geometries of radical cations differ substantially from geometries of neutral molecules. In the case of $\mathbf{3}^{\cdot +}$ an intermediate structure (λ_{max} = 600 nm) was intercepted which rearranged to the most stable structure (λ_{max} = 450 nm) both thermally or photochemically. Optimized geometries for radical cations involving multiple sulfur interactions were calculated.

Organic radical ions are important intermediates in a wide variety of electron-transfer reactions.[1] They are produced in chemical reactions and also on electrolysis, photolysis and radiolysis. Direct exposure of low-temperature glassy solutions to ionizing radiation is a particularly useful method of radical ion generation for optical studies. Both steady-state and time-resolved detection are feasible. We have recently established that low-temperature pulse radiolysis can be successfully applied to the studies of radical ion transformations with a very low activation barrier.[2] This technique has also been applied to the studies of conformation-dependent charge delocalization in aliphatic diamine radical cations.[3] It has been shown that the most stable structures characterized by the strongest σ-three-electron bonding interactions between nitrogen atoms are formed in conformationally driven processes which are described by dispersive kinetics.[4]

Formation of the σ-three-electron bonded radical cations generated from various thioethers is well established.[5] Evidence is also present for intramolecular σ-three-electron bonding interactions between sulfur atoms of some tetrathioether radical cations.[6] In this case multiple sulfur interactions are also feasible. Successive additions of appropriately placed *gem*-dimethyl groups to 1,4,8,11-tetrathiocyclotetradecane (**1**) as it is shown in the case of its derivatives bearing *gem*-dimethyl pairs at the 6- or at the 6- and 13-position (**2** and **3**, respectively) reveal important changes in macrocycle conformations.[7] Such changes are manifested by a significant increase in metal ion binding affinity.



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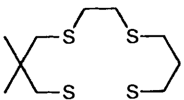

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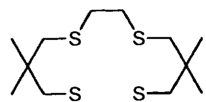

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The conventional drawings of the compounds **1**–**3** do not resemble the real conformations of these molecules. Crystalline **1** exists in three conformations, of which the two most stable are argued to be nearly identical α and β forms, which have nearly *anti* SCCS dihedral angles [∠S(1)CCS(4) = 176°, ∠S(8)CCS(11) = −176°],[8] and the SCCCS units also directed nearly *anti*, so the sulfurs are as far apart as possible, described as 'exodentate'[7] (the lone pairs point away from the centre of the ring). Desper and Gellman[7] showed that the tetramethyl compound **3** crystallizes instead in a conformation having *gauche* SCCS dihedral angles [∠S(1)CCS(4) = 71°, ∠S(8)CCS(11) = −71°], nearly *anti* CSCC dihedral angles, and *gauche* SCCCS units, placing the sulfur closer to each other adopting 'endodentate' configuration (the lone pairs point toward the centre of the ring). The dimethyl compound **2** may be described as being in an intermediate conformation with one *anti* and one *gauche* dihedral angle SCCS unit [∠S(1)CCS(4) = 58°, ∠S(8)CCS(11) = 173°]. Observed crystallographic structures are illustrated in Fig. 1.

This contribution presents electronic absorption spectra of radical cations generated radiolytically from **1**–**3** measured in the steady-state and time-resolved modes. It is shown that substantial changes in macrocycle conformations induced by the *gem*-dimethyl substitution are also manifested by distinctive spectroscopic and kinetics properties of intramolecularly interacting radical cations.

Results and Discussion

Absorption spectra of radical cations $\mathbf{1}^{\cdot +}$–$\mathbf{3}^{\cdot +}$ generated by γ-radiolysis in methylcyclohexane glass at 77 K are shown in Fig. 2. No new absorptions were detected for all three samples in the near-IR region (800–2200 nm). Due to restricted diffusion at low temperatures in methylcyclohexane glass, which was noticed above 100 K,[2d,9] intermolecular interactions between sulfur atoms are less likely. We believe that absorptions shown in Fig. 2 could, in a first approximation, represent the $\sigma \rightarrow \sigma^*$ transition in radical cations characterized by various intramolecular interactions between sulfur atoms. The energies of σ(SS) and the lone pair combination orbital of the same symmetry are close enough that they mix significantly, and the highest doubly occupied orbital in $[R_2S \cdots SR_2]^+$ is (σ–n) in character.[10] Relatively weak absorption observed at 460 nm with a long red tail for $\mathbf{1}^{\cdot +}$ [Fig. 2(*a*)] corroborated earlier observation of this species in hexane solution.[6] Unfortunately this absorption was too weak to be reliably detected by a low-temperature pulse radiolysis. Essentially a similar spectrum was detected for $\mathbf{2}^{\cdot +}$ [Fig. 2(*b*)], however the absorption observed was about five times stronger as compared to $\mathbf{1}^{\cdot +}$.

Absorption spectra monitored for $\mathbf{2}^{\cdot +}$ by pulse radiolysis are shown in Fig. 3. The spectrum detected a short time after the electron pulse [curve (*a*)] has no pronounced maximum in the observation range. The absorption appeared to grow with time,

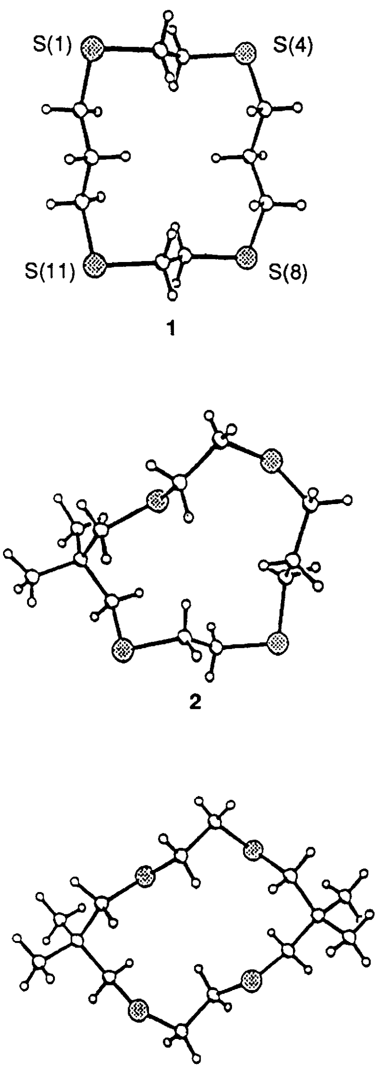

Fig. 1 Ball-and-stick representation of the crystallographically observed conformations for **1** (α form, ref. 8), **2** (ref. 7) and **3** (ref. 7)

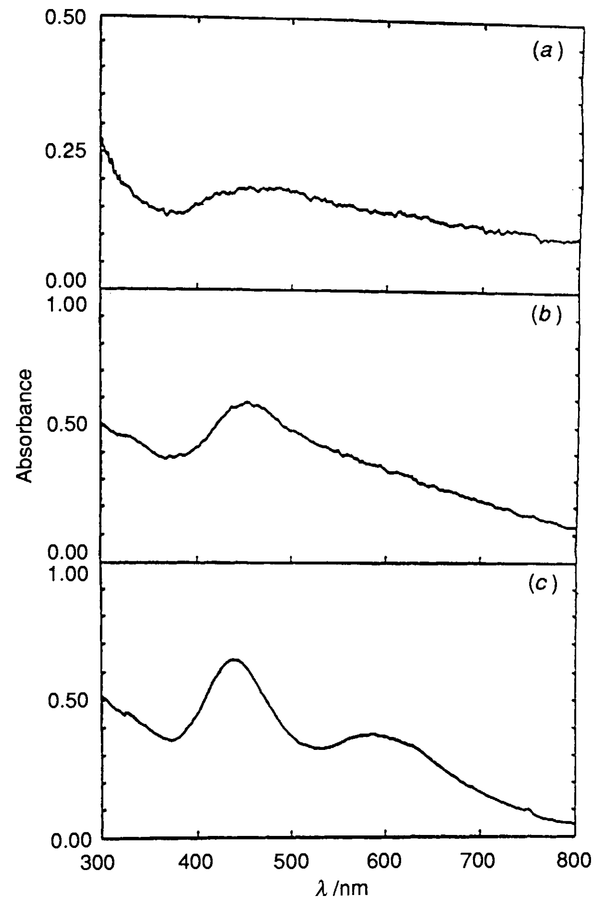

Fig. 2 Absorption spectra of γ-irradiated (^{60}Co) **1** (*a*), **2** (*b*) and **3** (*c*) (0.01 mol dm^{-3}) in glassy matrices of methylcyclohexane containing butyl chloride (1 mol dm^{-3}) at 77 K. The samples were 2 mm thick and received a radiation dose of 10^4 Gy.

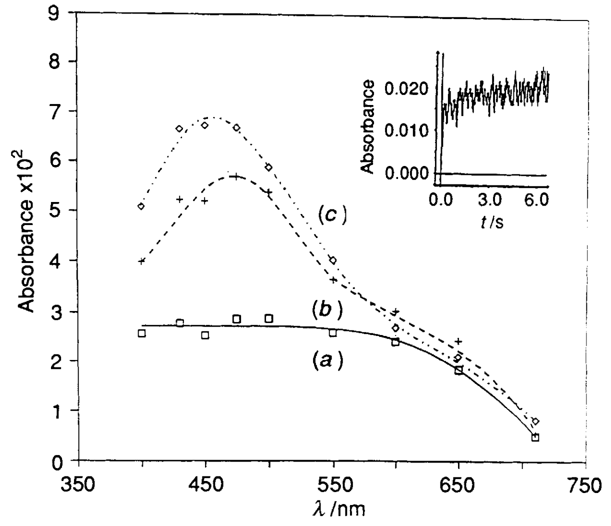

Fig. 3 Transient absorption spectra of $2^{\cdot+}$ at 84 K obtained (*a*) 3×10^{-4} s, (*b*) 0.68 s, (*c*) 6.2 s after the 4 μs electron pulse delivering a dose of 10^3 Gy. Inset: scope trace at 430 nm.

and 0.68 s after the pulse a spectrum with maximum at 470 nm was clearly seen [curve (*b*)]. At longer time-scale the spectrum was shifting toward blue with the final maximum detected at 430 nm [curve (*c*)]. Absorption growth detected at 430 nm is shown in the inset in Fig. 3. A delayed formation of the spectrum for $2^{\cdot+}$ indicates that the conformation of intramolecularly interacting radical cation is very much different from the conformation of the neutral molecule in glassy solution. After ionization, the radical cation initially formed retains the structure of the neutral parent and conformational motion monitored as the absorption change with time leads to a structure of the lowest energy characterized by the strongest interactions between sulfur atoms. This intramolecular rearrangement should, in principle, follow first-order kinetics. However, the experimental data do not follow such kinetics, as is shown in Fig. 4(*a*). The kinetics are more complex, suggesting a distribution of the initial conformations leading to distribution of the reaction rates. Therefore, we have analysed our results in terms of dispersive kinetics using the time-dependent rate coefficient in the form of eqn. (1), where coefficient

$$k(t) = Bt^{\alpha - 1} \qquad (1)$$

$0 < \alpha \leq 1$ measures the reactivity dispersion.[11] The first-order kinetic eqn. (2) with the time-dependent rate coefficient

$$-\mathrm{d}c/\mathrm{d}t = k(t)c \qquad (2)$$

[eqn. (1)] on integration gives the relation (3), which fits the

$$\ln(c/c_0) = -(B/\alpha)t^{\alpha} = -(t/\tau_0)^{\alpha} \qquad (3)$$

experimental results well. The best fit, as presented in Fig. 4(*b*), was obtained for $\alpha = 0.35$ and $\tau_0 = 0.23$ s^{-1}. A similar model

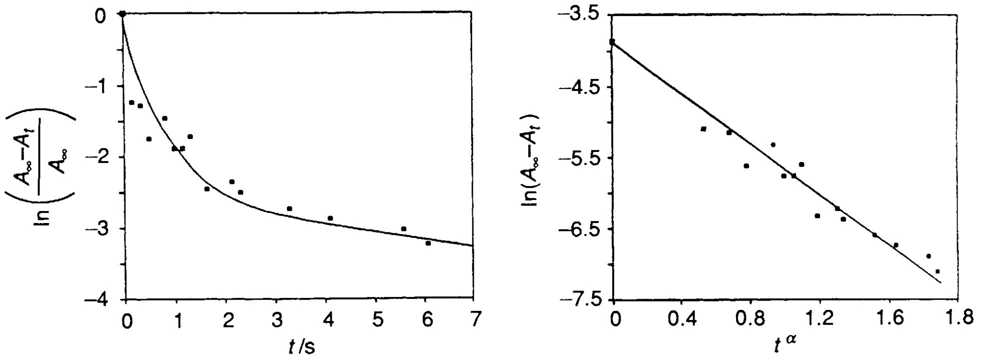

Fig. 4 Experimental data for the absorption growth of $2^{\cdot+}$ at 84 K presented in coordinates suitable for classical (*a*) and dispersive (*b*) kinetics. Wavelength monitored: 460 nm.

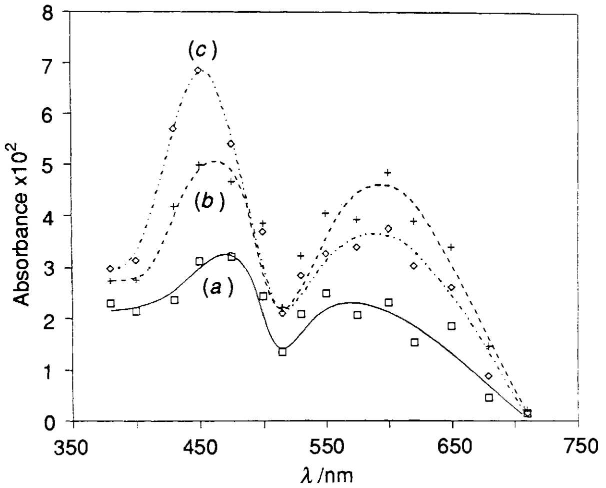

Fig. 5 Transient absorption spectra of $3^{\cdot+}$ at 84 K obtained (*a*) 3.1×10^{-4}, (*b*) 0.21, (*c*) 6.2 s after the 4 μs electron pulse delivering a dose of 10^3 Gy

for description of dispersive kinetics was already successfully applied to the analysis of kinetic data of conformational relaxation in diamine radical cations leading to structures with the strongest 3e–σ bonding interactions between nitrogen atoms.[4]

Especially interesting observations are made for $3^{\cdot+}$. In this case two pronounced absorption maxima at 450 and 600 nm are seen. Kinetic behaviour of the 450 and 600 nm bands are very much different as documented by the time-resolved detection of optical absorption spectra (Fig. 5). At early stages of observation both 450 and 600 nm bands are growing with time, however a 600 nm band seems to grow faster. At longer time-scale (above 1 s) the absorption with maximum at 600 nm decreases while the absorption band with maximum at 450 nm continues to grow (Fig. 6). Both decrease of 600 nm band and increase of 450 nm band in time-scale of seconds follow dispersive kinetics with relatively similar parameters ($\alpha = 0.90$ and $\tau_0 = 2.3$ s^{-1} for decrease of 600 nm band; $\alpha = 0.76$ and $\tau_0 = 1.8$ s^{-1} for increase of 450 nm band) suggesting that the interaction described by the 600 nm absorption is replaced by a stronger interaction assigned to the 450 nm transition. Similar changes could also be induced photochemically as is shown in Fig. 7. Upon photolysis with light of 590 nm the absorption band at 600 nm decreases with a parallel increase of absorption at 450 nm. Similar aspects of the *gem*-dimethyl substitution were discussed in analysing changes in optical spectra of radical cations generated from 2-substituted 1,3-dithiacyclopentanes.[12]

Simple estimation of the transition energies for optical spectra are complicated by the fact that Koopmans' theorem fails badly; the energy gap between the orbitals involved in the transition causing the band is not close to the transition energy. This effect appears to be principally caused by the difference in the occupancy of the orbitals involved; optical transitions are between doubly occupied and unoccupied virtual orbitals in closed shell species. Clark and coworkers[13] showed that for the special case of radical cation optical spectra, calculation of the energy gap between orbitals of equal occupancy in the related neutral species fixed at the geometry of the radical cation is a surprisingly good approximation to the observed transition energy for alkene radical cations, formally a one electron π-bonded system. Nelsen, Weinhold and co-workers[14] demonstrated that this approximation is also excellent at the *ab initio* level by comparing calculations of the transition energy for hydrazine radical cation (a 3e–π bonded system) with such NCG (neutral in cation geometry) predictions. They also showed that NCG predictions using semi-empirical calculations are useful for understanding the large changes in observed spectra of hydrazine radical cations as the alkyl substituent structure is changed. Clark has implemented such NCG calculations as a keyword in his VAMP AM1 program,[15] making such calculations easy to carry out. To see if NCG calculations might be of help in understanding the optical spectra of the SS 3e–σ bonded radical cations under consideration here, we have carried out NCG calculations for the acyclic, monocyclic and bicyclic (considering the S···S unit as a bond) systems from the extensive pulse radiolytic work of Asmus[5a,16] on such compounds. A reasonable correlation between the experimental band maxima and calculated NCG orbital separations was obtained.[17]

Both molecular mechanics and semi-empirical calculations make significant errors in prediction of conformations of neutral **1**–**3**. Neither MM2 nor AM1 calculations obtain optimized geometries which are near the experimental geometries, although the energy surface is so complex that we have certainly not examined it completely. Because AM1 does not properly calculate the minimum energy structure of the neutral compounds, it is unlikely that the energy differences between AM1 geometry optimized radical cation structures for these compounds are realistic. We nevertheless carried out such calculations on the radical cations to see if any insight into the intramolecular interactions between the sulfurs in these compounds could be attained. The AM1 calculations give the results that multiple sulfur interactions are preferred to structures with only one SS 3e–σ bond. To illustrate this, radical cation structures **A** to **D** found for $2^{\cdot+}$ using AM1-UHF are shown diagrammatically in Fig. 8; SS, distances ≤2.5 Å, indicating bonding, are shown as dotted lines; the structures are not planar. We failed to locate an energy minimum radical cation structure having interaction of all four sulfur atoms. Also

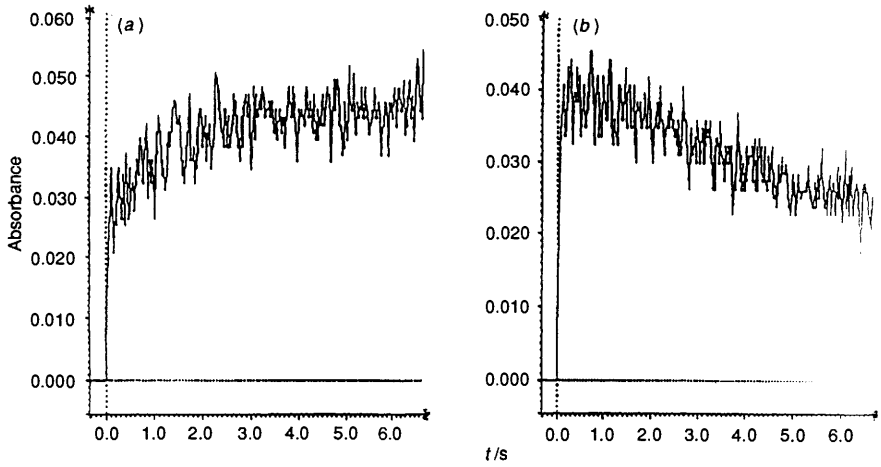

Fig. 6 Absorption changes of $3^{\cdot +}$ monitored at 450 nm (*a*) and at 600 nm (*b*)

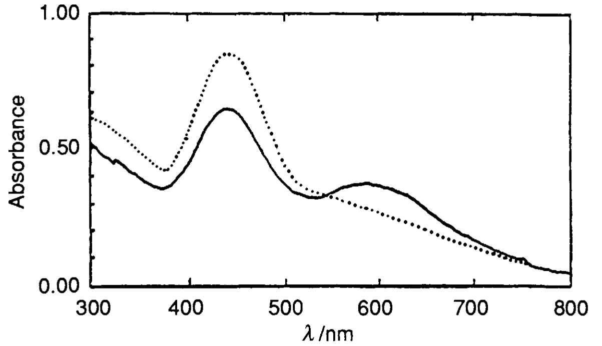

Fig. 7 Absorption spectra of γ-irradiated (^{60}Co) **3** at 77 K before photolysis (solid line) and after 45 min photolysis through a 590 nm interference filter (dotted line)

shown are predicted relative energies. 'Open' structures with no SS interaction were calculated to be much higher in energy (> 50 kcal mol^{-1})* and to have intense absorption in the IR region (*ca.* 1410, 2215, 3450 cm^{-1}). The relative energies are calculated to be sensitive to whether RHF or UHF optimizations are used, although the three SS interaction structure **A** was predicted to be most stable for both. It is unlikely that the relative energies are significant, but we think it is worth noting that a variety of complex intramolecular interactions between the sulfurs of polysulfide radical cations appears to be possible, and that the presence of multiple interactions would not necessarily be expected to result in longer wavelength absorption than would a single SS interaction.

Unfortunately we are not in a position to assign unambiguously structures to intramolecular complexes characterized by transitions at 450 and 600 nm. As shown, optimized geometries for multiple sulfur interactions can result in similar wavelength absorptions to those observed for single SS interactions and an assignment of the absorption bands to particular radical cations' structures would be very speculative at present. However, the conformation characterized by the 450 nm transition which is relatively far from the geometry of neutral molecule, and which AM1 is not even able to find efficiently, might most reasonably be the monobridged bicyclo[6.6.0] structure represented by **C**. If this is the case, AM1 is certainly not applicable here for comparison of relative energies.

To conclude, despite very different conformations for neutral molecules, radical cations generated from all three cyclotetrathioethers possess similarly located σ→σ* transition (near 450 nm) for the strongest interactions between sulfur atoms. It is clear, as convincingly shown for $2^{\cdot +}$, that the structure of radical cations may be very much different from the structure of neutral molecules. In the case of $3^{\cdot +}$ an intermediate structure was intercepted which rearranged to the most stable structure both thermally and photochemically.

Experimental

Cyclotetrathioethers **1–3** were synthesised by Desper and Gellman[7] and offered to us as a gift. Description of the pulse radiolysis system and procedure for the steady-state and time-resolved radiolytic measurements in hydrocarbon matrices are given elsewhere.[2,18] Photochemical reaction was carried out with a high-pressure mercury lamp HBO-200 (Narva) equipped with an interference filter LIF 590 (Zeiss Jena).

Acknowledgements

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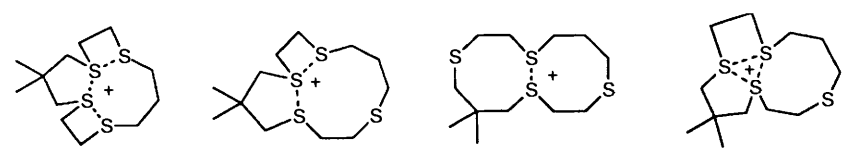

A	B	C	D
0	5.1	13.9	14.4

ΔH_f/kcal mol^{-1}

Fig. 8

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* 1 cal = 4.18 J.

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