[14] All new compounds were characterized by ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry, C,H,N analysis, and/or high-resolution mass spectrometry.
[15] Grigg et al. suggested that polar solvents favor ligand dissociation and thereby accelerate the catalysis.[10g] However, in the examples studied by us, cyclotrimerizations occurred in toluene, which may be due to an enhanced reactivity of the *N*-1-alkynylamides for cyclotrimerizations in comparison with that of the diynes studied by Grigg.
[16] Additional monosubstituted alkynes, such as phenyl acetylene and 1-pentyne, undergo cyclotrimerization reactions with the diynes **4a**, **3i**, and **3j**. Further studies are in progress to explore the mechanistic factors responsible for the selectivity, as well as cyclotrimerization studies with nickel and cobalt catalysts.
[17] The structural assignment of compound **12a** is based on 2D-NMR experiments (H, H- and C, H-COSY, as well as HMBC) and distinct NOE relationships. We would like to thank Prof. Dr. L Ernst (Technische Universität Braunschweig) for the NOE measurements.

Tricyclopropylamine and Its Radical Cation**

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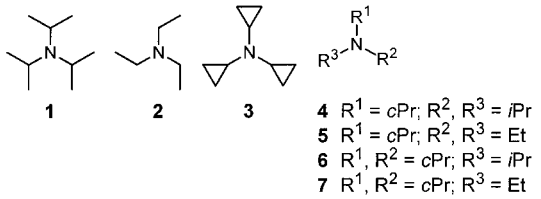
Dedicated to Professor George Olah on the occasion of his 70th birthday

In view of the report by Bock et al.[1] that triisopropylamine (**1**) is nearly planar at the nitrogen atom, and can, therefore, be oxidized unusually easily to a persistent radical cation, tricyclopropylamine (**3**) appeared to be a particularly interesting target for synthesis. In terms of the steric demand, a cyclopropyl group is significantly smaller than an isopropyl group[2] and slightly larger than an ethyl substituent, but is a far better electron donor to adjacent electron-deficient centers than any other alkyl group.[2, 3] Thus the three cyclopropyl groups in **3** should stabilize its radical cation $\mathbf{3}^{\bullet+}$ exceptionally well, so that the latter might be formed even more readily than the radical cations of **1** and triethylamine (**2**), just as the tricyclopropylmethyl cation emerges as a particularly stable tertiary carbenium ion.[4] Since neither S_N1 nor S_N2 displacements on cyclopropyl derivatives are easily achieved, **3** could not be prepared by straightforward cyclopropylation of cyclopropylamine. Fortunately, however, we were able to develop a new general synthesis of cyclopropyldialkylamines from acid dialkylamides[5, 6] which was readily adapted for the preparation of **3**.[7]



X-ray crystal structure analyses of tricyclopropylamine **3** at 130 K (Figure 1 A)[9] and its hydrochloride at 200 K[11] revealed that both have about the same pyramidal arrangement at the nitrogen atom ($\Sigma(\sphericalangle$C-N-C$) = 330.3^\circ$). Moreover, the orientation of all three cyclopropyl groups with respect to the lone pair on the nitrogen atom in **3** and to the N–H axis in **3**·HCl is exactly the same as that determined by computational[12, 13] and microwave-spectroscopic[13] studies on gas-phase cyclopropylamine. A gas-phase electron diffraction (GED) structure analysis of **3** established that the molecule in the free state has essentially the same conformation (Figure 1 B)[14] as in the crystal.

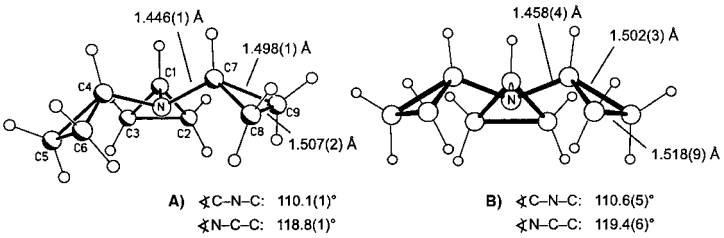


Figure 1. Structures of **3** in the crystal at 130 K (A)[9] and in the gas phase (B).[14] The distances and angles given for crystalline **3** are mean values; the interplanar angles between the plane C1,C4,C7 to the planes N,C1 and center of C2–C3; N,C4 and center C5–C6; N,C7 and center C8–C9 are 97.5, 83.9, and 93.8°, respectively. Shortest H···H distance 2.380(58) Å.

In this conformation, electron density can be delocalized from the nitrogen lone pair into the symmetric components of the cyclopropyl LUMOs.[12] In accord with the greater bulk of the isopropyl compared to the cyclopropyl groups, the C–N bonds in **3** (1.446(1) Å) are shorter than those in **1** (GED: 1.460(5) Å[3], X-ray structure analysis at 84 K: 1.469(1) Å[15]),

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while the proximal C–C bonds (1.498(1) Å, mean value) in the cyclopropyl groups are shorter than the distal ones (1.507(2) Å, mean value); however, the latter are not longer than in unsubstituted cyclopropane.[16] The shortest non-bonded H···H distances in **3** are 2.380(58) Å. According to density functional theory (DFT) calculations at the RB3LYP/6-31G(D) level, which reproduce very well the experimental geometry of **3** (Figure 2), the shortest H···H separations in

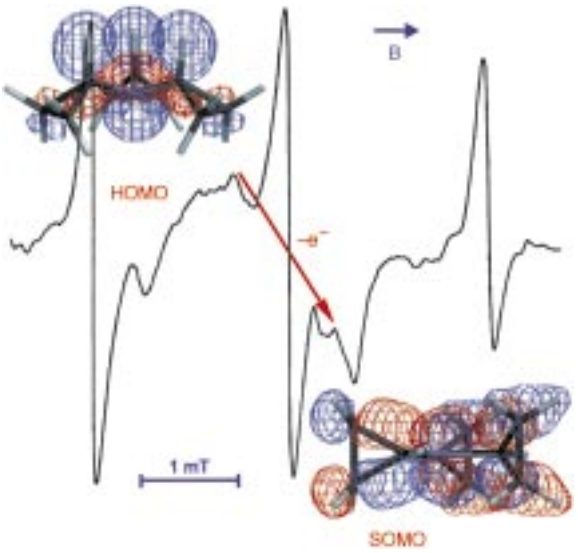

Figure 2. EPR spectrum of tricyclopropylamine radical cation $\mathbf{3}^{\bullet+}$ in a $CF_2ClCFCl_2$ matrix at 125 K (black curve). Minimum-energy structures of **3** with a plot of the highest occupied molecular orbital (HOMO) and its radical cation $\mathbf{3}^{\bullet+}$ with its semi-occupied orbital (SOMO), according to RB3LYP/6-31G(D) and UB3LYP/6-31G(D) calculations, respectively (colored structures). Selected bond lengths [Å] and angles [°]: **3**: N–C 1.449 Å, C–C(prox.) 1.506, C–C(dist.) 1.510, shortest H···H 2.383; C-N-C 111.1, C-C-N 119.8. $\mathbf{3}^{\bullet+}$: N–C 1.426, C–C(prox.) 1.531, C–C(dist.) 1.490, shortest H···H 2.176 Å; C-N-C 120.0, C-C-N 122.2.

C_{3v}-symmetrical **3** are 2.383 Å, and in planar C_{3h}-symmetrical **3** they would be 2.235 Å, not prohibitively short in view of the shortest experimental H···H distances in **1** of 2.216 Å.[15] The C_{3v} structure of **3**, with its pyramidal nitrogen environment was found to be 16.2 kcal mol^{-1} more stable than the C_{3h} conformation which is planar at nitrogen. The stabilizing interaction between the nitrogen lone pair and the e_S-type Walsh orbitals of the three adjacent cyclopropyl groups in the C_{3v}-symmetrical form is apparent in the HOMO of the molecule (Figure 2).

In agreement with the degree of pyramidality and the orientation of the cyclopropyl groups in **3** (which do not favor donor interactions with a partially vacant $N^{\bullet+}$ orbital), the vertical first ionization energy (IE_v) is 1.26 eV higher than that of **1**. The first band in the He^I photoelectron spectrum of **3** with a half-width of 0.70 eV is broader than that for dicyclopropylisopropylamine (**6**), cyclopropyldiisopropylamine (**4**), and cyclopropyldiethylamine (**5**),[17] which indicates a larger than usual difference between vertical and adiabatic ionization energy of these and other tertiary amines. The IE_v of **3** was found to fall in line with the values for **6**, **4**, and **5**, as compared to triisopropylamine (**1**) (Table 1). Each

Table 1. Experimental[a] and computed[b] vertical first ionization energies (IE_v) for tertiary amines **1**–**7**.

Amine	IE_v(exp.) [eV]	IE_v(calcd) [eV]	Σ∢C-N-C [°]
1	7.18[3]	7.13	348.6[15]
2	8.08[19]	8.01	ca. 330[c]
3	8.44	8.26	330.3
4	7.79	7.56	339.9[20]
5	8.23	7.90	338.8[d]
6	8.14	7.93	338.9[d]
7	8.39	8.17	334.1[d]

[a] Determined from He^I-photoelectron spectra.[18] [b] B3LYP/6-311+G**/B3LYP6-31G* level. [c] As the crystal structure of **2** is characterized by a disorder phenomenon, only a range of C-N-C angles (107–112.1°) is reported in ref. [15]. [d] Computed values (RB3LYP/6-31G(D)).

additional cyclopropyl group that replaces an isopropyl or an ethyl group consistently raises the σ(N)-ionization energy of the N lone pair, with the biggest jump occurring between **1** and **4** or **1** and **5**. This behavior is in accord with changes in pyramidalization at the nitrogen atom (Table 1).[19] As amine radical cations are inherently planar, the IE_v of **1**, which has a planarized nitrogen environment, (∢C-N-C 116.2° according to an X-ray structure analysis at 84 K[15]) is much less than that of **3**, with its 110.1(1)° C-N-C bond angles. This is shown by model computations on trimethylamine: The IE_v for the pyramidal minimum energy geometry with a C-N-C angle of 111.6° (exp. 110.7°[15]) is 8.36 eV (exp. 8.53 eV[19]), a value close to that of **3**, whereas IE_v calculated for a planar NMe_3 (7.44 eV) is similar to that of **1**. Moreover, the vertical ionization of **3** results in a radical cation, the frozen geometry of which would preclude effective hyperconjugative stabilization by the cyclopropyl substituents. While steric effects very well account for the planarization at the nitrogen atom of **1**, they cannot be the only reason for the perpendicular orientation of cyclopropyl groups in cyclopropylamines. An X-ray crystal structure analysis of **4** at 163 K revealed that its two isopropyl groups adopt the "tongue and grove" conformation as in planarized **1**, yet the cyclopropyl group has the perpendicular orientation as in **3**, although the average C-N-C bond angle is 113.3°.[20, 21] Thus, the cyclopropyl group prefers to accept electron density from the adjacent nitrogen atom into its LUMO.

Consistent with the high gas-phase ionization energy of **3**, the radical cation $\mathbf{3}^{\bullet+}$ could not be generated by oxidation of **3** with antimony pentafluoride in dichloromethane, a procedure which succeeded with trialkylamines having an IE_v value lower than about 8 eV.[3, 22] γ-Irradiation of **3** in a "mobile" $CF_2ClCFCl_2$ matrix by a ^{60}Co source at 77 K led to an anisotropic EPR spectrum of a radical cation. On raising the temperature toward the softening point of the matrix, the spectrum became increasingly isotropic; it disappeared above 130 K. An essentially isotropic spectrum, taken at 125 K (Figure 2), exhibited a 1:1:1 triplet due to the ^{14}N nucleus with the coupling constant a_N of 2.01 ± 0.01 mT ($g = 2.0037 \pm 0.0001$).[23] This spectrum is consistent with that expected for the radical cation $\mathbf{3}^{\bullet+}$. From the observed line width (peak-to-peak) of 0.18 mT, the unresolved hyperfine splitting a_H^{β} by the three methine β-protons was estimated as 0.06–0.08 mT, assuming an a_H^{γ} value of 0.05 mT for the twelve methylene γ-protons.

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The ^{14}N-coupling constant a_N close to 2 mT is characteristic of radical cations of trialkylamines with a planar geometry at the nitrogen atom, that is with a predominant $2p_z$-character of the singly occupied N orbital,[3, 22, 24] while the small value of a_H^{β} indicates that the methine β-protons lie in the nodal plane of this orbital. Such a value is strongly reduced relative to the corresponding coupling constant a_H^{β} of 0.148 mT, observed recently by us in a highly resolved EPR spectrum of $\mathbf{1}^{\bullet+}$.[22]

Indeed, as confirmed by DFT calculations at the UB3LYP/6-31G(D) level, the minimum-energy geometry of $\mathbf{3}^{\bullet+}$ has C_{3h} symmetry (17.0 kcal mol^{-1} more stable than a nonplanar C_{3v} geometry) with the three cyclopropyl groups in the bisected orientation (Figure 2). In the C_{3h}-symmetrical conformation the radical cation $\mathbf{3}^{\bullet+}$ can thus gain stability from the ideally oriented cyclopropyl groups.

In addition, the computed EPR-coupling constant (using the Perdew exchange correlation potential and the IGLO-III basis set with the SOS-DFPT[25] method[26]) of the three equivalent β-protons in (C_{3h})-$\mathbf{3}^{\bullet+}$, 0.08 mT, agrees well with the experimentally derived value of 0.06 – 0.08 mT, but differs strongly from the result (5.3 mT) for nonplanar (C_{3v})-$\mathbf{3}^{\bullet+}$. Thus, the computational results, in the context of the EPR-spectroscopic phenomena, disclose a dramatic conformational change on going from **3** to $\mathbf{3}^{\bullet+}$. To the best of our knowledge, this is the first case of a tertiary amine for which direct experimental evidence for such a structural change has been obtained. Planarization is a general phenomenon upon ionization of any amine, but conformational changes, like those observed for the cyclopropyl substituents in **3**, are quite unusual.[22]

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[2] The steric effects of alkyl and cycloalkyl groups have been quantified with varying success, using linear energy relationships. One of the steric constants schemes which accounts for the steric effect of a cyclopropyl group rather well is the list of $\mathscr{S}_i$(R) values (H. D. Beckhaus, *Angew. Chem.* **1978**, *90*, 633 – 635; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 593): $\mathscr{S}_i$(R) = 0.00 (Me), 0.86 (Et), 2.29 (*i*Pr), 3.82 (*t*Bu), 1.33 (*c*Pr), 1.81 (*c*Pent).

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[9] The liquid, colorless tricyclopropylamine (**3**) was crystallized at 227 K in a Lindemann capillary (0.3 mm diameter) by the in situ technique with an IR laser as described before,[10] and diffraction data for a cylindrical crystal were collected at 130 K on a Nicolet R3 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. Cell dimensions $a = 7.906(3)$, $b = 11.896(4)$, $c = 9.236(3)$ Å, $\beta = 98.53(3)^\circ$, $V = 859.0(5)$ Å^3, monoclinic, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 1.061$ Mg m^{-3}, $2\theta_{max} = 80^\circ$, $\mu = 0.062$ mm^{-1}, 7402 intensities collected, 4190 independent ($R_{merg} = 0.024$), 3166 observed ($F_o > 4\sigma F$), structure solution and refinement on F^2 with Siemens SHELXTL V. 5.03, 151 parameters for anisotropic refinement for all atoms except hydrogen atoms which were located in a difference Fourier map and given isotropic temperature parameters without further constraints. *R*1 (observed data) = 0.0464, w*R2* (all data) = 0.1376, GOF(F^2) = 1.023, $w^{-1} = \sigma^2(F_o^2) + (0.0867p)^2 + 0.01p$ with $p = (\max F_o^2 + 2F_c^2)/3$, maximum residual electron density 0.26 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101130. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[20] Full details of this crystal structure analysis of **4** and the preparations of **4** – **7** will be published separately. R. Boese, D. Bläser, H. Winsel, A. de Meijere, unpublished results.

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Resolution of Racemic 1,2-Dibromohexafluoropropane through Halogen-Bonded Supramolecular Helices**

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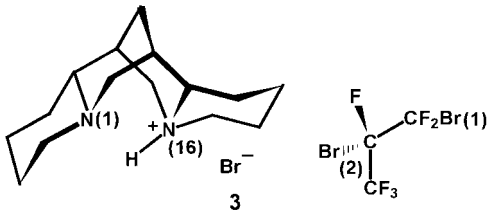
The chemical and physical properties of functionalized perfluorocarbons (PFCs) differ substantially from those of corresponding hydrocarbons (HCs).[1] The unique combination of properties expected for enantiopure PFC derivatives is likely to present unprecedented applications and to yield important information,[3] but this anticipation can hardly be verified as enantiopure PFCs are a virtually unknown class.[6]

As a consequence of the unique features of PFC derivatives, specifically tailored methodologies have to be developed to make enantiopure PFC derivatives available. The approach to obtain optically pure compounds by resolving their racemic forms through formation of diastereoisomeric and noncovalent adducts is well established in the HC series. This procedure could be applied to the resolution of racemic PFC derivatives by means of enantiopure HC resolving agents if an adequate PFC – HC interaction is identified. Here we describe the first example of a pairing that proves effective in the case of dibromoperfluoroalkanes. We report that the electron donor – acceptor interaction between enantiopure trialkylammonium hydrobromides (electron donor) and racemic perfluoroalkyl bromides (electron acceptor) is robust and selective enough to allow the resolution of the latter compounds through PFC – HC cocrystal formation.

We have already described the attractive intermolecular interaction between perfluoroalkyl iodides and trialkylamines.[7, 8] The term "halogen bond" has been proposed[9] for this interaction owing to its similarities with the hydrogen bond. The halogen bond is specific, directional, and strong enough to overcome the low affinity existing between PFC and HC derivatives, driving the self-assembly of the two motifs into solid and crystalline noncovalent copolymers starting from individual components which are liquid at room temperature. An electron donor – acceptor interaction occurs also between perfluoroalkyl bromides and nitrogen, oxygen, and sulfur atoms present in HC compounds, but this interaction is weaker that that with perfluoroalkyl iodides.[10] Thus it is not surprising that no solid copolymer was obtained starting from racemic 1,2-dibromohexafluoropropane and various chiral and enantiopure diamines (e.g. (−)-1,2-diaminocyclohexane, (+)-Tröger's base, (−)-sparteine).[11]

In contrast, when enantiopure (−)-sparteine hydrobromide (**1**) and racemic 1,2-dibromohexafluoropropane (**2**) were mixed in chloroform, the yellow cocrystal **3**, made up of **1** and (*S*)-**2** exclusively, was isolated (Figure 1). The architecture



3

Figure 1. Schematic representation of the interaction between units of **1** and **2** in the cocrystal **3** through halogen bonds. Selected bond distances [Å] and angles [°]: Br(1)···Br⁻ 3.369(1), Br(2)···Br⁻ 3.260(1), C–Br(1) 1.910(12), C–Br(2) 1.959(8), N(16)···Br⁻ 3.548(6), N(1)···Br⁻ 3.622(6); C–Br(1)···Br⁻ 173.6(4), C–Br(2)···Br⁻ 178.4(3), Br(1)···Br⁻···Br(2) 143.01(4). The two bromine atoms bound to a given Br⁻ ion belong to distinct PFC molecules. Standard sparteinium atom numbering is adopted.

of **3** (Figure 2), as determined by single-crystal X-ray diffraction,[14] clearly evidences the propensity towards segregation of the functionalized PFC and HC motifs.[18] On the other hand, the high cohesion of the cocrystal **3** is demonstrated by its thermal stability (m.p. 105 °C, decomp.), when compared to the low melting point of racemic **2** (− 95 °C), and by the 4% molar volume reduction with respect to the pure components (24 Å^3) on cocrystal formation.

The driving force towards cocrystallization is the Br⁻···Br–C intermolecular interaction between bromide ions, working as electron donors (i.e. bases), and carbon-bound bromine atoms, working as electron acceptors (i.e. acids).[20] Each bromide ion bridges a primary and a secondary bromine of two distinct PFC units **2**, each of which is well ordered through bonding to two bromide ions. Thus enantiopure, infinite twofold helices parallel to the *b* axis develop (Figure 3). The resolution of **2** is the result of a highly specific inclusion in a chiral crystal with a halogen-bonded helical arrangement. This process maximizes the transfer of information from the HC to the PFC units.

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[**] Perfluorocarbon-Hydrocarbon Self-Assembly, Part 5. Part 4: reference [7].

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