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Structure and Proton-Donor Ability of *N*-(1-Trifluoromethylsulfonylamino-2,2,2-trichloroethyl)-acrylamide

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Abstract—Quantum-chemical calculations (B3LYP/6-311G**) of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide $CF_3SO_2NHCH(CCl_3)NHC(O)CH=CH_2$ (**I**) in the isolated state revealed four local minima corresponding to the conformers with the syn- and antiperiplanar orientation of the C=O and N–H bonds in the amide fragment, two of which containing the intramolecular C(O)NH···O=S or SO_2NH···O=C hydrogen bonds. Judged from the data of IR spectroscopy and dielectrometry, compound **I** in inert media exists predominantly in the form of conformer with antiperiplanar amide fragment and free NH group. Its self-associates in molecular crystals and solutions are formed by hydrogen bonds SO_2NH···O=C. Spectroscopic acidity of compound **I** determined as the value of Δν(NH) upon interactions with DMF in CCl_4 is higher than that of *N*-methyltrifluoromethanesulfonamide.

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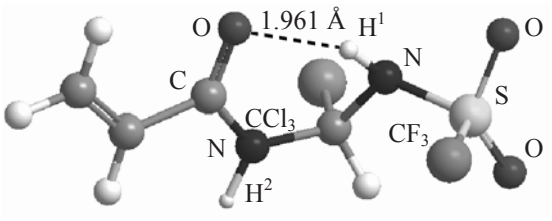
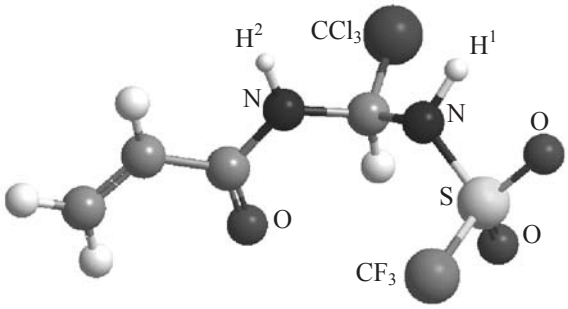
In continuation of the experimental and theoretical studies of the molecular and supramolecular structure of trifluoromethanesulfonamide and its derivatives as strong NH-acids [1–9], it was of interest to expand the circle of objects by including functionally substituted compounds possessing several acidic and basic centers in one molecule. Earlier, we have investigated three examples of such compounds: trifluoro-*N*-(2-phenylacetyl)methanesulfonamide $CF_3SO_2NHC(O)CH_2Ph$ having one acidic and two different basic centers [7], 2- and 2,5-bis(1-trifluoromethanesulfonylamino-2,2,2-trichloroethyl)pyrroles having two different acidic and one or two identical basic centers [8], and *N*-[(trifluoromethylsulfonyl)aminomethyl]acetamide $CF_3SO_2NH·CH_2NHCOCH_3$ having two different acidic and two different basic centers [9]. The former compound exists in the form of two conformers with the syn- and antiperiplanar amide group and forms associates both with the NH···O=S and the NH···O=C bonds [7]. In trifluoromethanesulfonamide derivatives of pyrroles the intra-molecular hydrogen bonds NH···O=S and CH···O=S are formed affecting the protonodonor ability of these compounds with respect to Lewis bases [8]. In compound $CF_3SO_2NHCH_2NHCOCH_3$ only the intramolecular hydrogen bond SO_2N–H···O=C is realized, so, it retains the ability to self-association with participation of the C(O)NH bonds in condensed media [9].

In the present work, by the use of IR spectroscopy, dielectrometry and quantum chemical calculations including calculation of frequencies of normal vibrations, the structure of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide $CF_3SO_2·NHCHCCl_3NHC(O)CH=CH_2$ **I** is studied in the isolated and crystal state and in inert media, and its protonodonor ability (spectroscopic NH-acidity) is estimated from the shift of the ν(NH) band of stretching vibrations upon the intermolecular interaction with DMF in the carbon tetrachloride solution.

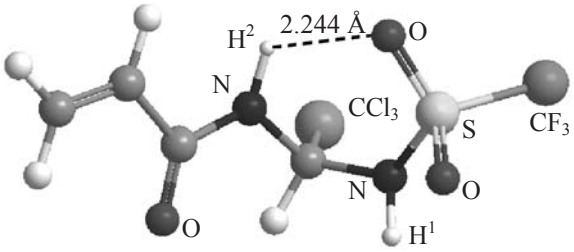
Quantum-chemical calculations of the isolated molecule of compound **I** revealed the presence of four conformers corresponding to the minima on the potential energy surface (Fig. 1). As one should expect, more stable turned out to be conformers **Ia–Ic** with the antiperiplanar *ap*-orientation of the NH and CO bonds of the amide group. The most stable of them conformer **Ia** contains an intramolecular hydrogen



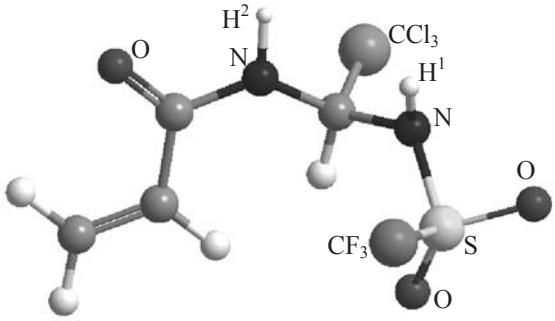
Ia, ΔE = 0 kcal mol^{-1}, μ = 6.21 D,
ν(NH^1) = 3424 cm^{-1}, ν(NH^2) = 3639 cm^{-1}



Ib, ΔE = 0.48 kcal mol^{-1}, μ = 5.82 D,
ν(NH^1) = 3580 cm^{-1}, ν(NH^2) = 3625 cm^{-1}



Ic, ΔE = 2.73 kcal mol^{-1}, μ = 1.07 D,
ν(NH^1) = 3584 cm^{-1}, ν(NH^2) = 3611 cm^{-1}



Id, ΔE = 4.33 kcal mol^{-1}, μ = 1.07 D,
ν(NH^1) = 3574 cm^{-1}, ν(NH^2) = 3590 cm^{-1}

Fig. 1. Molecular structure of conformers of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide (**I**).

bond formed by the sulfonamide group NH and the carbonyl oxygen atom and having the H···O distance of 1.961 Å. The chelate six-membered ring in compound **Ia** has the *twist-boat* conformation with planar CH–NH–C=O fragment. A high calculated dipole moment of this conformer (6.21 D) must cause its preferable stabilization also in solutions, especially in polar media. Conformer **Ib** is only by 0.48 kcal mol^{-1} less stable than conformer **Ia** in spite of the fact that both NH group in it are free. Apparently, the stability of compound **Ib** is due to the reduced intramolecular contacts, that allows interaction of the acidic proton of the CCl_3CH group (as proved by its large low-field chemical shift by δ 6.3 ppm [10]) with the oxygen atoms of the amide and sulfonyl groups: the CH···OC and CH···OS distances are equal to 2.276 and 2.429 Å, respectively. Conformer **Ib** is also characterized by a large value of dipole moment (5.82 D). Conformer **Ic** contains the intramolecular hydrogen bond NH···O=S (2.244 Å) formed by the amide NH group. Its energy is by 2.73 kcal mol^{-1} higher than that of conformer **Ia** but the dipole moment is substantially lower (1.07 D). Conformer **Id** with the synperiplanar *sp*-orientation of the amide group is by 4.33 kcal mol^{-1} less stable than conformer **Ia** and has the lowest dipole moment (0.91 D). It should be mentioned that all conformers have reduced contacts NH···Cl with the interatomic distance H···Cl in the range of 2.73–2.91 Å.

In the IR spectrum of a diluted solution of compound **I** in CCl_4 (C ~10^{-4} mol l^{-1}) (Fig. 2, the table) two intense bands of the stretching vibrations of the amide and sulfonamide NH groups of monomeric molecules occur at 3434 and 3380 cm^{-1}, respectively, and there is a wide low-frequency band ν(NH) at 3106 cm^{-1} characterizing its self-associates. It was reasonable to assume that in nonpolar solvent CCl_4 dominates the conformer having either the minimal energy or the lowest dipole moment. Conformer **Ia** fits the first condition. According to calculations, the frequency of ~3220 cm^{-1} should correspond to the vibration band of its NH group involved in the intramolecular hydrogen bond SO_2NH···O=C [$\Delta\nu$(NH) = $\nu(NH_{free}) - \nu(NH_{ass})$ ~160 cm^{-1}, Fig. 1]. However, the

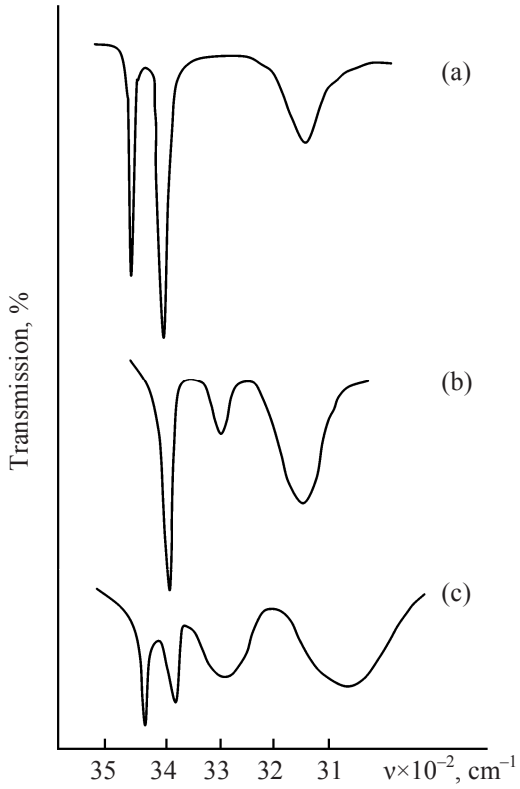


Fig. 2. IR spectra of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide. (a) Solution in CCl_4, $C \approx 10^{-4}$ mol l^{-1}, d = 5 cm; (b) in KBr; (c) solution in CCl_4 with addition of DMF.

IR spectrum of compound **I** in CCl_4 does not contain any band in this region. The best correspondence to the experimental difference Δν(NH) = 54 cm^{-1} between the ν(NH) values of the amide and sulfonamide groups was obtained for the Δν(NH) value calculated for conformer **Ib** close in energy to the most stable conformer **Ia** and equal to 45 cm^{-1} (Fig. 1). The assignment of the observed bands to free NH groups of conformer **Ib** is also supported by the fact that these values are close to the calculated and the experimental values of the difference between the frequencies of vibrations of the NH groups of bis(acrylamido)-methane $(CH_2{=}CHCONH)_2CH_2$ (**II**) and *N*-methyl-trifluoromethanesulfonamide CF_3SO_2NHMe (**III**) [Δν(NH) 58 and 46 cm^{-1}, respectively) (Fig. 1, the table). For conformer **Ic** having a low dipole moment although less energetically favorable, the calculated value of this difference is lower [Δν(NH) = 26 cm^{-1}] due to formation of the intramolecular hydrogen bond C(O)NH···O=S.

Stretching vibration frequencies of N–H bonds, ν(NH), cm^{-1} and the difference between the values ν(NH) of free and associated NH groups, Δν(NH), cm^{-1} in IR spectra of *N*-(1-trifluoromethylsulfon-ylamino-2,2,2-trichloroethyl)acryl-amide (**I**), N,*N*-(methylenebis-acrylamide) $(CH_2{=}CHCONH)_2CH_2$ (**II**), and *N*-methyltrifluoromethanesulfonamide (**III**)

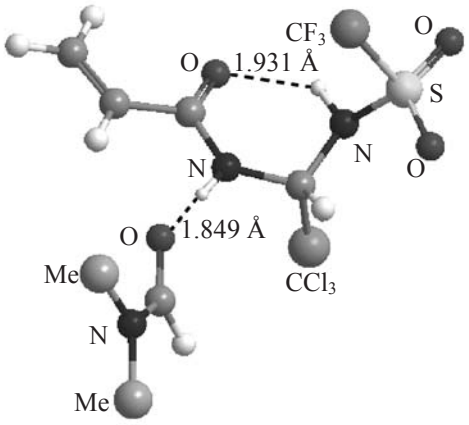
Comp. no.	CCl_4	CH_2Cl_2	KBr	DMF in CCl_4 solution
	ν(NH)			Δν(NH)
I	3434	3413	3382	140
	3380	3330	3293	300
	3106		3125	
II	3450	3437	3308	140
III	3406	3380	3300[a]	272

[a] In thin film.

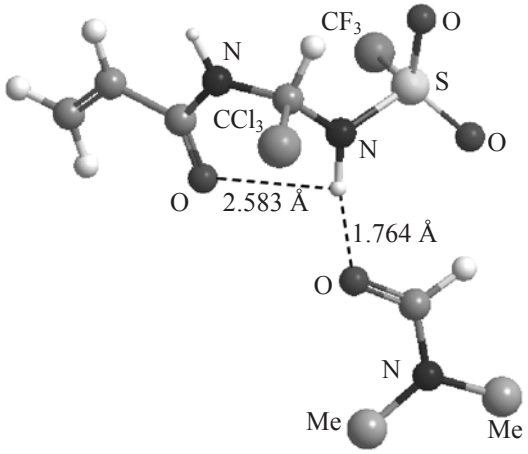
An independent confirmation of stabilization of conformer **Ib** in an inert medium was obtained by measuring the dipole moment (μ) of compound **I** in benzene. The experimental value of μ 4.5 D is most close to the calculated for conformer **Ib** (5.82 D). In the IR spectra of solutions of compound **I** in benzene and in more polar CH_2Cl_2 the vibration bands of the free NH groups of the amide and sulfonamide fragments exert a low-field shift by 20–30 and 50–60 cm^{-1}, respectively. The presence of conformer **Ic** along with conformer **Ib** in an inert medium is unlikely due to substantial difference of their energies ΔE = 2.25 kcal mol^{-1}.

A wide band ν(NH) with maximum at 3106 cm^{-1} in the spectrum of solution of compound **I** in CCl_4 (Fig. 2, the table) corresponds to the NH groups of the sulfonamide fragment participating in the formation of intermolecular hydrogen bonds with the carbonyl group oxygen atom, which is more basic than the sulfonyl oxygen atom. The intermolecular nature of these bonds is proved by a decrease of intensity of this band upon dilution of the solution up to its full disappearance at $C \sim 10^{-5}$ mol l^{-1}. A wide intense band at 3125 cm^{-1} in the IR spectrum of crystalline compound **I** (Fig. 2, the table) corresponds to the ν(NH) vibrations of its sulfonamide group involved in the $SO_2NH\cdots O{=}C$ bond formation. A higher frequency of this vibration in the crystal as compared to the solution, Δν(NH) = 19 cm^{-1}, is indicative of formation of chain polyassociates in the molecular crystal. Intermolecular hydrogen bonds forming these poly-associates are less strong than hydrogen bonds of the same nature forming cyclic dimers in nonpolar CCl_4; similar relations have been obtained by us earlier for hydrogen bonds NH···O=S forming the chain and cyclic dimers of trifluoromethanesulfonamide and its

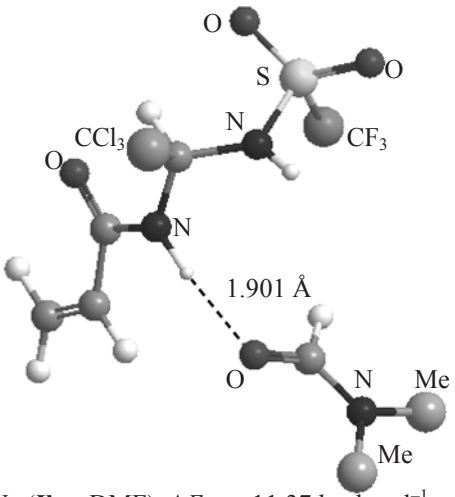
N-methylsubstituted (**III**) [1, 2]. An intense narrow band [ν(NH) = 3382 cm^{-1}, $\Delta\nu_{1/2}$ ~2 0 cm^{-1}] in the IR spectrum of crystalline compound **I** is due to vibrations of its free NH group of its amide fragment, that can be explained by a lower acidity of the latter as compared with the sulfonamide NH group. A low-frequency shift of this band in going from nonpolar solvent CCl_4 (3434 cm^{-1}) to more polar CH_2Cl_2 (3413 cm^{-1}) and further to the crystal (3382 cm^{-1}) is due to an increase of dielectric constant of the medium and crystal packing effects. With this, a weak wide band at 3293 cm^{-1} may correspond either to the ν(NH) vibrations of the sulfonamide NH group involved in the intermolecular hydrogen bonding with the sulfonyl oxygen atom or the amide group bound to the C=O group oxygen atom. Thus, the band ν(NH) 3300 cm^{-1} belongs to self-as-sociates of acrylamide(II) (crystal) and *N*-methyltrifluoromethanesulfonamide **III** (neat liquid) with intermolecular hydrogen bonds NH···O=C and NH···O=S, respectively. Therefore, compound **I** in the crystalline state and in inert media predominantly exists in the form of conformer **Ib** with the sulfonamide NH group involved in the formation of intermolecular hydrogen bond SO_2NH···O=C, and the free amide NH group. In molecular crystals of compound **I**, besides, small fraction of self-associates is present formed by the SO_2NH···O=S and/or C(O)NH···O=C bonds.



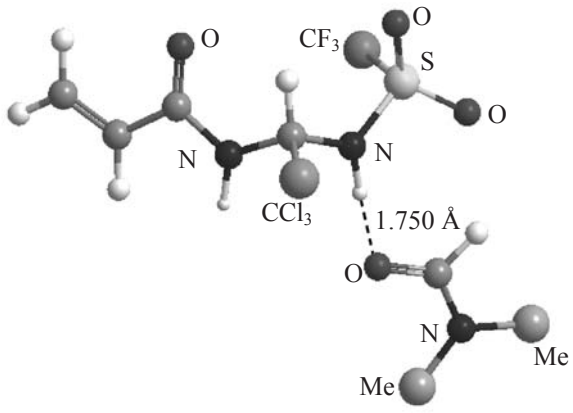
IVa (**Ia** + DMF), ΔE_c = –11.70 kcal mol^{-1}
ΔE = 1.30 kcal mol^{-1}, Δν(NH) = 252 cm^{-1}



IVb (**Ia** + DMF), ΔE_c = –7.72 kcal mol^{-1}
ΔE = 5.28 kcal mol^{-1}, Δν(NH) = 299 cm^{-1}



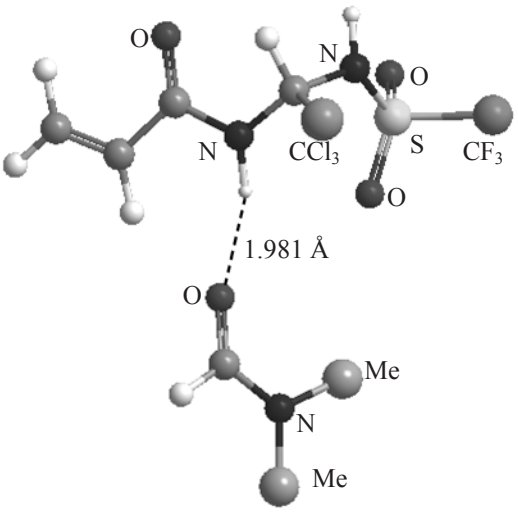
IVc (**Ib** + DMF), ΔE_c = –11.37 kcal mol^{-1}
ΔE = 2.10 kcal mol^{-1}, Δν(NH) = 235 cm^{-1}



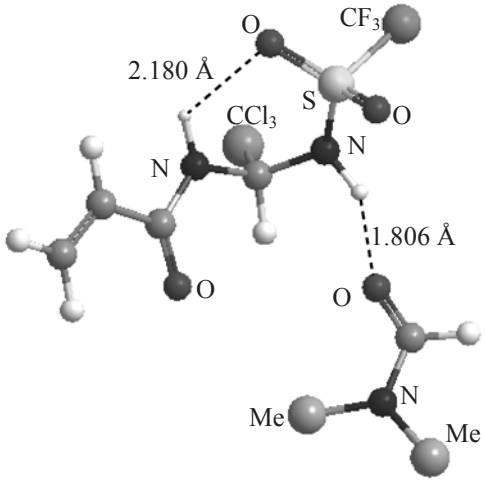
IVd (**Ib** + DMF), ΔE_c = –13.47 kcal mol^{-1}
ΔE = 0 kcal mol^{-1}, Δν(NH) = 480 cm^{-1}

Fig. 3. Structure of molecular complexes of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide **I** with DMF.

Fig. 3. (Contd.)



IVe (**Ic** + DMF), ΔE_c = –8.58 kcal mol^{-1}
ΔE = 7.16 kcal mol^{-1}, Δν(NH) = 128 cm^{-1}



IVf (**Ic** + DMF), ΔE_c = –13.20 kcal mol^{-1}
ΔE = 2.55 kcal mol^{-1}, Δν(NH) = 264 cm^{-1}

Conformational structure of the isolated molecule of compound **I** and the presence of two acidic centers creates conditions for the formation of different types of H-complexes in the presence of an external base. We performed calculation of complexes of DMF with three most stable conformers **Ia–Ic** with the *ap*-orientation of the amide group for coordination of the base both to the amide and the sulfonamide NH group (Fig. 3). According to calculations, the most stable was complex **IVd** formed by conformer **Ib** with the sulfonamide NH proton involved in the intermolecular hydrogen bond and the shortest interatomic distance *r* (O···H) 1.750 Å (Fig. 3). In the absence of intramolecular hydrogen bond in the protonodonor [conformers **Ib**, **Ic**], complexation to the sulfonamide NH group is energetically preferable and leads to an increase of the complexation energy (ΔE_c) and twice as large shifts Δν(NH) (Fig. 3, complexes **IVc–IVf**). In the presence of the intramolecular hydrogen bond SO_2NH···O=C in the initial protonodonor (conformer **Ia**), it is practically completely broken upon the formation of complex with the external base at the sulfonamide NH group leading to destabilization of complex **IVb** relative to **IVa**. Frequency shifts Δν(NH) for the amide and sulfonamide NH groups in this case are only slightly different (Fig. 3).

Experimentally, the protonodonor ability of the NH groups in compound **I** was determined from the values of spectroscopic acidity Δν(NH) as the difference between the values of ν(NH) of free NH groups in an inert solvent CCl_4 and associated NH groups in H-complexes formed in the solution upon addition of DMF as a standard Lewis base (see table).

In the IR spectrum obtained after addition of DMF to a diluted solution of compound **I** in CCl_4, two vibrations bands of associated NH groups are observed (Fig. 2). The shifts of their frequencies Δν(NH) relative to the vibration bands of the free sulfonamide or amide NH group are 300 and 140 cm^{-1}, respectively. Twice as large experimental spectroscopic acidity of the sulfonamide group is in nice agreement with the calculated above shifts Δν(NH) for SO_2NH and C(O)NH groups. It may be noted that protondonor ability of the amide NH group of compound **I** is the same as in acrylamide **II** for both compounds the value of Δν(NH) is 140 cm^{-1}. At the same time, spectroscopic acidity of the proton of sulfonamide group of compound **I** is higher than of *N*-methyltrifluoromethanesulfonamide **III**, for which Δν(NH) is 272 cm^{-1} (see the table). With this, *N*-methyltrifluoromethanesulfonamide itself, as shown by us earlier [6],

in H-complexes with protophilic solvents acts as a strong hydrogen bond donor, exceeding 4-fluorophenol and being second only to 4-nitrophenol.

EXPERIMENTAL

Synthesis of *N*-(1-trifluoromethylsulfonylamino-2,2,2-trichloroethyl)acrylamide **I** is described in [10].

IR spectra of the compounds were registered on a Varian 3100 FT-IR spectrophotometer. Dielectric permeability of its solutions in benzene was measured on an Epsilon instrument (Angarsk, AO OKBA) at 1 MHz frequency. Dipole moments were calculated by the Higashi formula [11].

Quantum chemical calculations, including vibrational calculations, were performed at the B3LYP/6-311G** level of theory with full geometry optimization using the Gaussian 03 program suite [12].

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