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Infrared Spectrum and Structure of 2-Thienyl-N-methylfulleropyrrolidine

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Abstract—The IR and ^{1}H NMR spectra of 2-thienyl-*N*-methylfulleropyrrolidine are studied. The complete interpretation of the spectra is carried out on the basis of density functional theory calculations. Conformational composition is analyzed by means of both computational and experimental methods.

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Photogalvanic cells and artificial photosynthesis systems based on donor–acceptor diads are a rapidly advancing field of research in new energy sources [1–3]. The operation principle of these devices is as follows: absorbing a light quantum, one component (donor) of the diad enters an excited electronic state; relaxation from this excited state involves electron transfer to the other component (acceptor) to produce a charge-separated state. In this context, fullerenes are interesting for their high electron affinity: they can act as efficient electron acceptors in photogalvanic cells [4]. Many diads of fullerenes C_{60} with phorphyrins, polythiophenes, chlorins, ferrocene, and other donors have been synthesized. The Prato reaction is one of the most frequently used methods for diad synthesis: this is the dipolar addition reaction of C_{60} with azomethinylides [1], which produces *N*-methylfulleropyrrolidines of the general formula $C_{60}(CH_2)_2N(CH_3)CHR$ with donor substituent groups R at the heterocycle.

The nonplanar configuration of the pyrrolidine cycle, the internal rotation of group R, and the equatorial–axial isomerism of the methyl group make the coexistence of several conformers possible for such diads. Evidently, the properties of the diad depend above all on the relative location in space of the donor and acceptor fragments; this location can change from one conformer to another.

Despite a significant interest in *N*-methylfulleropyrrolidine-based diads, structural and conformations investigations (in particular, by means of spectroscopic methods) for such molecules have not been performed. This work is intended to study the structure and spectra of 2-thienyl-*N*-methylfulleropyrrolidine (TMFP, Fig. 1) using computational and experimental methods.

EXPERIMENTAL AND COMPUTATION PROCEDURES

The synthesis of TMFP is described in [5]. The IR spectrum of TMFP was recorded as KBr pellets on a Bruker IFS-113v FTIR spectrometer in the range 400–4000 cm^{-1} with a 0.5 cm^{-1} resolution. The ^{1}H NMR spectrum was measured on a Varian VXR-400 spectrometer using a carbon sulfide/acetone-d_6 (9 : 1) solvent.

The molecular geometry was optimized and the IR spectra and proton shifts were calculated using Priroda software [6] in terms of the PBE generalized gradient approximation [7] and a three-exponent basis set supplemented with two sets of *d*-type polarization functions (TZ2P). Auxiliary computations in terms of the B3LYP hybrid functional and in terms of the Möller–Plesset second-order perturbation theory (MP2) were carried out using the GAMESS program package [8].

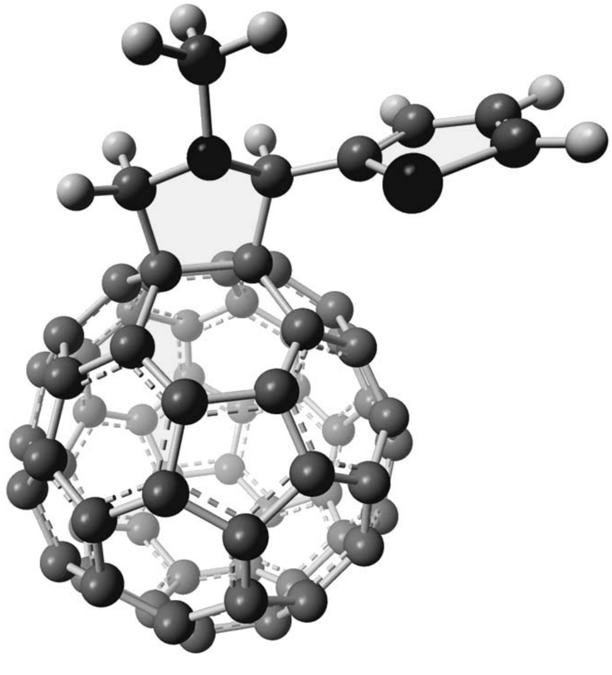

Fig. 1. Model of a TMFP molecule.

Direct and inverse vibrational problems were solved using the DISP program package [9]; the quantum-mechanical force fields obtained as a result of the computations were converted to the internal coordinate system, which was constituted by all bond length changes, bond angles, and nonplanar and torsion coordinates.

RESULTS AND DISCUSSION

Computation of the Geometry and Relative Energies of Conformers and Tranformation Barriers

During the optimization of the TMFP molecular geometry, eight nonequivalent minima were located on the potential energy surface; this was due to the inversion of the heterocycle, the possibility of the internal rotation of the thiophene moiety, and the equatorial or axial position of the methyl group relative to the root-mean-squares plane of the pyrrolidine ring. Each of the eight conformers in addition has one enantiomer.

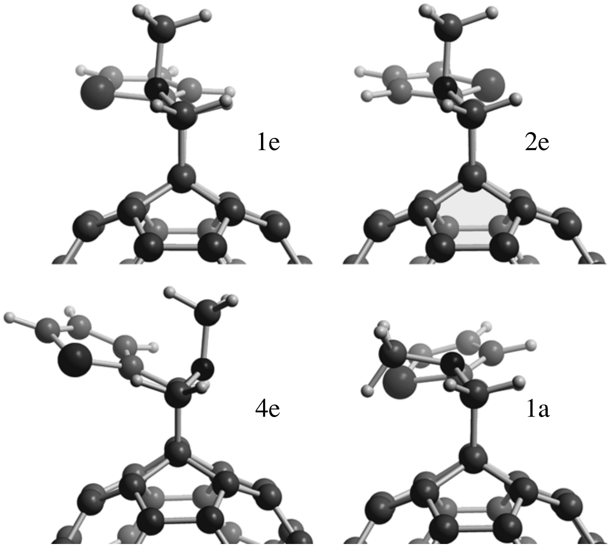

Fig. 2. Configurations of four TMFP conformers.

Figure 2 displays some structures that correspond to minima in the potential energy surface and that illustrate the routes of possible intramolecular structural transformations: from the most stable conformer (see below), which is denoted as **1e** and which is characterized by the equatorial position of the CH_3 group, conformer **2e** can be obtained by turning the thiophene ring plane by some 40° with respect to the NCC plane (the sulfur atom lies more closely to the nitrogen atom) with the internal rotation of the $–C_4SH_3$ fragment by 180°. Heterocycle inversion (with the turn of the thiophene moiety) produces conformer **4e**. Conformer **1a** is distinguished by the axial position of the CH_3 group (and by some change in the rotation angle of the $–C_4SH_3$ fragment). Functionality significantly distorts the geometry of the fullerene cage near its attachment place. The longest bond (1.605 Å) is the C–C bond along which the heterocycle is attached; this value, which is noticeably greater than the length of an ordinary bond in the carbon cage, is indicative of significant strains near the functionality. Adjacent ordinary bonds of the cage become 0.05–0.1 Å longer; the other bonds of the fullerene cage remain practically unchanged. Table 1 displays some geometric parameters and the relative energies of the eight potentially possible TMFP conformers computed using the PBE/TZ2P method with the energy of the zero vibrational level taken into account. From Table 1 it follows that the conformers with the equatorial orientation of the methyl group have higher stability; of them, the conformers in which the thiophene substituent lies opposite to the lone pair of the nitrogen atom are less profitable. The two most stable conformers (**1e** and **2e**), as computed, have a small energy difference (2.4 kJ/mol with account of the energy of the zero vibrational level); therefore, their

Table 1. Geometric parameters (*E*, deg) and relative energies (kJ/mol) for eight conformers of a TMFP molecules from PBE/TZ2P computations

Parameter	1e	2e	3e	4e	1a	2a	3a	4a
E(PBE/TZ2P)	0.0	2.4	18.3	16.4	27.7	26.0	31.4	28.3
C^2–N^1	1.462	1.462	1.457	1.457	1.466	1.466	1.467	1.467
C^3–N^1	1.455	1.455	1.451	1.451	1.447	1.446	1.448	1.450
C^6–N^1	1.465	1.465	1.469	1.464	1.461	1.461	1.458	1.459
C^3–C^4	1.557	1.556	1.558	1.558	1.599	1.600	1.585	1.587
C^4–C^5	1.605	1.605	1.608	1.607	1.596	1.596	1.598	1.596
C^5–C^6	1.590	1.590	1.589	1.589	1.632	1.632	1.636	1.632
C^6–C^7	1.495	1.499	1.515	1.514	1.496	1.497	1.512	1.507
$\chi(N^1, C^3, C^4, C^5)$	26.1	26.8	–27.2	–27.4	22.2	22.1	–24.8	–23.5
$\chi(N^1, C^6, C^5, C^4)$	–28.4	–28.3	24.3	24.3	–26.5	–26.7	15.6	16.2
$\chi(N^1, C^6, C^7, S^8)$	–39.8	141.3	115.2	–54.7	–67.7	110.5	160.0	–36.6
$\chi(C^2, N^1, C^3, C^4)$	–170.1	–170.9	177.7	178.7	91.6	91.6	–93.6	–94.5

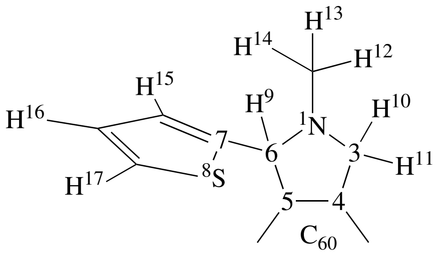

Fig. 3. Atom numbering used in the work.

coexistence is expected: the equilibrium composition calculated for 298 K is a mix of conformers **1e** and **2e** in the 74 : 26 proportion with infinitesimal concentrations of the other conformers.

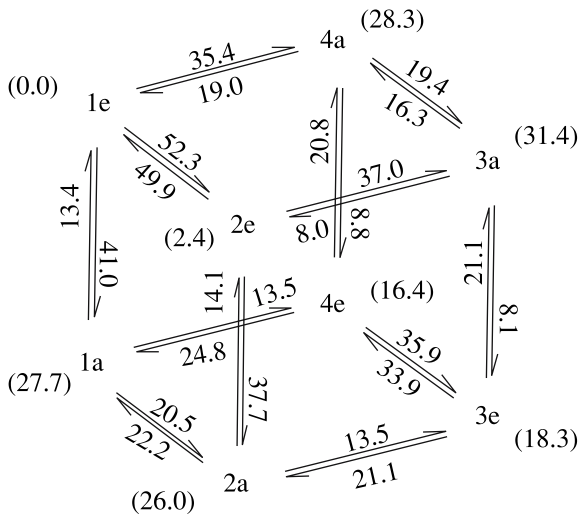

Fig. 4. Transition routes and barriers between TMFP conformers (kJ/mol). In parentheses, the energies of conformers are indicated.

In order to estimate the energy of possible conformational transformations in a TMFP molecule, we built one-dimensional sections of the potential energy surface for the internal coordinates that correspond to the conformational transitions: the dihedral angle SCCN for the rotation of the thiophene substituent, a linear combination of the dihedral angles (C^2, N^1, C^3, C^4) and (C^2, N^1, C^6, C^5) for describing the movement of the methyl group, and the combination of these angles with the angles (N^1, C^3, C^4C^5) and (N^1, C^3, C^5C^4) for the heterocycle inversion. The atomic numbering used in this work is shown in Fig. 3. Next, we optimized the geometry of transition states; this enabled us to estimate the transition barrier heights. The routes and energies of possible transitions are displayed in Fig. 4. It follows from Fig. 4 that the transformation barriers, counted starting from the pertaining minima, for all types of movement lie in an approximate range from 20 to 50 kJ/mol (cf. 20.8–41.1 kJ/mol for equatorial ⟷ axial transitions, 19.4–52.3 kJ/mol for the internal rotation of the thiophene radical, and 21.1–36.9 kJ/mol for the inversion of the pyrrolidine cycle). The highest value is for the transition between the two most stable conformers, likely because of the steric hindrances to the rotation of the thiophene substituent around the C_6–C_7 line; these hindrances appear due to the small distance to the fullerene cage.

Table 2. Experimental and calculated chemical shifts for proton signals from TMFP

Proton	Chemical shift, ppm				
	calculated				observed
	1e	2e	3e	4e	
9	5.31	5.13	6.07	6.35	5.32
10	4.71	4.69	4.41	4.44	5.00
11	4.18	4.16	5.07	5.29	4.30
12	2.98	2.90	2.53	2.48	
13	2.73	2.69	2.57	2.63	
14	1.75	1.76	2.01	2.25	
CH_3 (avg.)	2.49	2.45	2.37	2.45	2.91
15	7.00	7.35	7.57	6.97	7.02
16	6.60	6.76	6.95	6.71	7.04
17	7.05	6.82	6.90	7.16	7.39

^1H NMR Spectra of TMFP

The number of signals recorded in the ^1H NMR spectra of TMFP matches the number expected for one conformer; this can be due to either the existence of a single species in solution or the averaging of signals from several conformers as a result of rapid transitions between them; see, e.g., [10]: in the ^{19}F NMR spectra of the compound $C_{60}FCF_3$ recorded at room temperature, there was a single average signal from the fluorine atoms of the CF_3 group with the barrier to its internal rotation of some 50 kJ/mol.

More data about the conformational composition of the compound can be gained from the comparison of the observed chemical shifts for proton signals with the values calculated using the GIAO-PBE/TZ2P procedure for the four most stable conformers (Table 2). An analysis of the data compiled in Table 2 brings us to the conclusion that the values calculated for conformer **1e** best of all agree with the experiment.

IR Spectra for TMFP

The measured IR spectrum of TMFP is displayed in Fig. 5. As a result of the lack of symmetry and the large number of atoms in the molecule, the spectrum is very complex; this is virtually a continuum spectrum in the

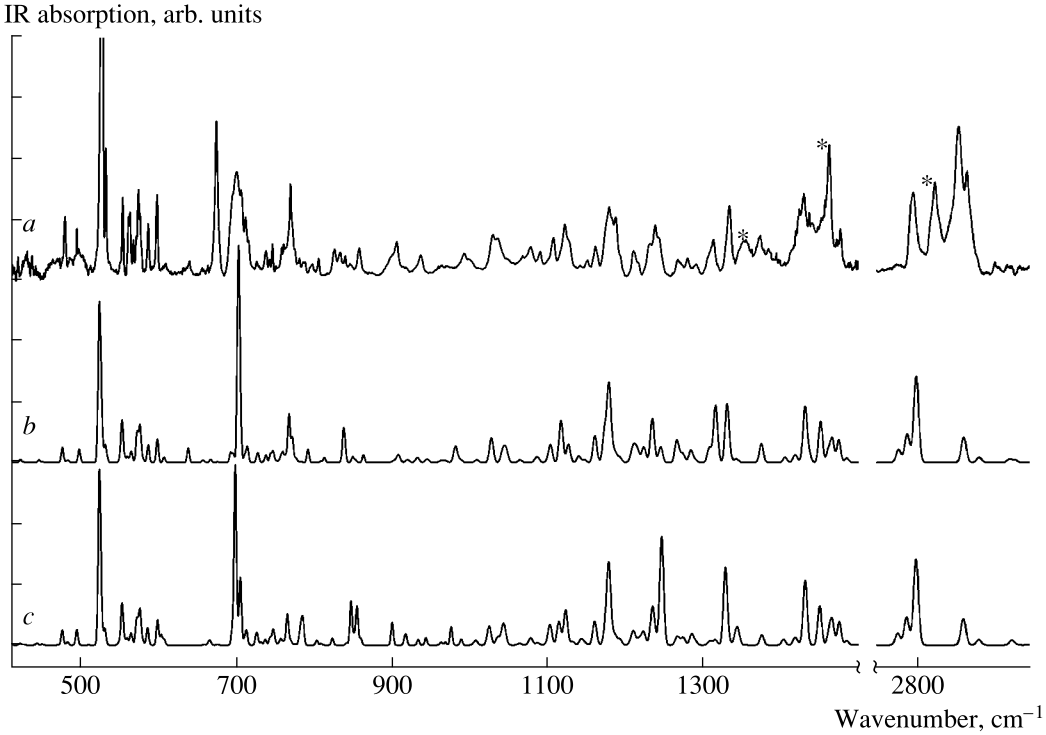

Fig. 5. (*a*) Measured and (*b*, *c*) simulated IR spectra for TMFP conformers: (*b*) **1e** and (*c*) **2e**. Asterisks mark lines associated with impurity solvents.

region 400–1650 cm^{-1}, accompanied by several bands in the region of the CH stretching vibrations.

Assignment was carried out on the basis of the quantum-mechanical computations of force fields and the line intensities. Previously [11], we showed that using the PBE generalized gradient functional [7] in combination with the three-exponent basis set supplemented with two sets of *d*-type polarization functions, one can reach a satisfactory fit of the vibrational spectra of cage carbon structures without force field scaling; the mean-square deviation of the calculated frequencies from the measured values was 6 cm^{-1}. However, force field scaling can appear necessary for this method to adequately fit the force fields of the moieties attached to the fullerene cage. In order to obtain necessary scaling factors, we carried out provisional computations of vibrational spectra for thiophene and *N*-methylpyrrolidine model molecules. For the thiophene molecule, we borrowed the spectrum assignment from work [12]; as a result of solving the inverse problem by means of the Pulay technique [13], we obtained the scaling factors in the narrow range from 0.9670 to 1.0949. For the *N*-methylpyrrolidine molecule, in contrast, the literature assignment [14] leads to inadequate overestimates of

Table 3. Scaling factors for the force fields of an *N*-methylpyrrolidine molecule

Coordinate	Scaling factor					
	spectrum assignment [14]			this work		
	B3LYP/ 6-311G**(*d*, *p*)	MP2/cc-pVTZ	PBE/TZ2P	B3LYP/ 6-311G**(*d*, *p*)	MP2/cc-pVTZ	PBE/TZ2P
QCC	1.3570	1.2845	1.3743	1.0658	1.0179	1.0801
QCN	1.2496	1.2354	1.3314	0.9741	0.9759	1.0432
γHCC	0.8780	0.8567	0.8709	0.9632	0.9345	0.9058
γHCN	0.8655	0.8497	1.1021	0.9074	0.8781	1.0756
γCNC	0.7654	0.7030$_3$	0.8144	1.0475	0.9431	1.0903
γNCC	0.4441	0.5014	0.9405	1.0263	1.0646	1.0231
rms_{ov}, cm^{-1}	18.2	23.0	17.5	15.8	24.5	14.2

Table 4. Calculated and observed vibrational frequencies and assignment of IR spectra for TMFP

TMFP		C_{60}		Addend		
ν_{obs}, cm^{-1}	ν_{calcd}, cm^{-1}	ν, cm^{-1}	assignment	ν, cm^{-1}	assignment (NMP)	assignment (thiophene)
3067	3074			3086		νCH
2976	2982			2958	νCH	
2920	2935			2877	νCH	
2782	2764			2771	νCH	
2738	2738			2754	νCH	
1558	1563	1567	$H_g(8)$			
1538	1531			1504		νCC + δHCC
1518, 1507, 1489	1518, 1508, 1485	1525 1499	$F_{2u}(5)$ $G_g(6)$			
1471	1461			1458	δHCH	
1462	1451			1448	δHCH	
1439	1436			1409		νCC + δHCC
1436, 1429, 1424, 1419, 1412	1431, 1429, 1419, 1405	1429, 1425, 1418	$F_{1u}(4)$	1418	δHCH + δHCN	
			$H_g(7)$			
			$G_u(6)$			
1334	1335	1342	$H_u(6)$			
1305	1308	1311	$G_g(5)$			
1280, 1267, 1231	1275, 1266, 1222	1270 1252	$F_{1g}(3)$			
			$H_g(6)$			
1244	1245			1256		δHCC
1231, 1210	1222, 1211	1214	$H_u(5)$			
1217	1215			1150	δHCC + δHCN + νCN	
1194, 1182, 1179, 1162, 1151	1193, 1177, 1173, 1161, 1148	1182 1168	$F_{1u}(3)$			
			$F_{2u}(4)$			
1188	1179			1150	νCN + δHCC + δHCN	
1128	1127			1115	δHCC + δHCN	
1122, 1108, 1079, 1068	1117, 1104, 1084, 1065	1099 1079	$H_g(5)$			
			$G_g(4)$			
1090	1085			1085		δHCC + νCC
1029	1028			1039	δHCN + νCC + νCN	
1001, 918, 905	988, 920, 908	973 962	A_u			
			$G_u(4)$			
993, 936	982, 933	956	$F_{2u}(3)$	965	νCC + δCCC + δNCC + δHCN	
918	920			943	νCC	
905, 898	908, 902			898		ρCH
858	863			872		νCS + δCCC + δSCC
846, 839, 833, 826	853, 849, 839, 837	827	$F_{1g}(2)$	839		νCS
				867		ρCH

Table 4. (Contd.)

TMFP		C_{60}		Addend		
ν_{obs}, cm^{-1}	ν_{calcd}, cm^{-1}	ν, cm^{-1}	assignment	ν, cm^{-1}	assignment (NMP)	assignment (thiophene)
805, 798, 793	813, 810, 808	796	$F_{2g}(3)$			
788, 785, 780, 775	792, 776, 772, 771	775	$G_u(3)$			
			$H_g(4)$			
769, 761, 758, 751, 746	767, 763, 759, 751, 747	757	$F_{2g}(2)$	751		νCS + δCCC + δSCC
		757	$G_g(3)$			
		753	$G_u(2)$			
746, 737, 726	747, 738, 728	739	$H_u(4)$			
742	744			787	δHCC + δHCN	
715, 711, 706, 700	714, 711, 706, 702	712	$F_{2u}(2)$ $H_g(3)$	715		ρCH
694	692			683		ρCH
694, 656	692, 657	668	$H_u(3)$			
640	638			608		δCCC + δSCC + νCS
609	607			572	δCCC + δNCC + νCC + νCN	
598	598			615	δCCC + δNCC + δCNC	
576, 571, 567, 553	576, 572, 564, 553	575	$F_{1u}(2)$ $G_g(2)$			
586, 536	586, 533			565		τCCCC + τSCCC
561, 550	555, 550	553	$F_{2g}(1)$			
553, 536	553, 533	533	$H_u(2)$			
532, 526	524, 523	526	$F_{1u}(1)$			
495	498			452		τCCCC + τSCCC
488, 485, 479	484, 482, 476	496 485	$A_g(1)$ $G_g(1)$			

scaling factors for the coordinates of C–C and C–N bonds. Therefore, we carried out additional computations of the molecular force field at the B3LYP/6-311G(d,p), MP2/cc-pVTZ, and PBE/TZ2P levels and proposed another assignment of the spectra. The scaling factors computed in terms of the specified approaches using the literature or our assignment of the spectra are listed in Table 3.

The factors listed in the last column of Table 3 (together with the respective factors for the thiophene moiety) were then used for scaling the quantum-mechanical force fields computed for the two most stable TMFP conformers. The results of the computation are compared to the experimental data in Fig. 5. The spectra simulated for conformers **1e** and **2e** are very similar; some distinctions are only observed in the regions of 830–870 and 1200–1350 cm^{-1}. The measured spectrum is slightly better fitted by the spectrum simulated for conformer **1e**; thus, we can infer that this conformer dominates in crystals of the compound.

The assignment of the bands observed in the spectrum (Table 4, first column) was carried out by means of normal-coordinate analysis; for clarity, the assignment was also carried out in terms of the normal vibrations of the starting fullerene, thiophene, and *N*-methylpyrrolidine molecules; their vibration frequencies are also listed in the table. The full set of the calculated vibration frequencies for TMFP and the results of the normal-coordinate analysis are available from the authors.

In the region 400–800 cm^{-1}, the strong lines are due to fullerene vibrations (Table 4). The components of the $F_{1u}(1)$ mode of the starting fullerene are mixed with components of the $H_u(2)$ mode; they are observed as very strong bands within a narrow range of 526–532 cm^{-1}. The group of medium-intensity peaks at 553–598 cm^{-1} is assigned to the derivative vibrations $F_{1u}(2)$ mixed with $F_{1g}(1)$ and $G_g(2)$ modes. The components of the fivefold degenerate modes $H_g(3)$, $H_u(4)$, and $H_g(4)$ with small contributions of threefold and fourfold degenerate modes appear in the spectrum with moderate or low intensities at 694–715, 726–746, and 758–788 cm^{-1}, respectively. The very strong band at 700 cm^{-1} is due to the out-of-plane vibration of hydrogen atoms in the thiophene moiety; the C–S stretching vibration is observed at 858 cm^{-1} and has a medium intensity (Table 4). In the starting compound, these vibrations are observed at 722 and 872 cm^{-1}, respectively [12].

The vibrations of the fullerene cage appear in the range 800–1100 cm^{-1}, frequently mixed with the stretching vibrations of the pyrrolidine moiety. The strongest bands in the range 1100–1600 cm^{-1} are due to the C–C and C–N stretching vibrations and the HCC and HCN bending vibrations in the addends (Table 4). The $F_{1u}(3)$ and $F_{1u}(4)$ modes of fullerene appear as medium-intensity and high-intensity bands at 1143–1194 and 1424–1436 cm^{-1}, respectively. The other vibrations of the carbon cage are virtually unobserved in this spectral range, except for several medium-intensity lines at 1210–1238 cm^{-1} (the $H_u(5)$ and $H_g(6)$ modes of fullerene) and 1473 cm^{-1} (the $A_g(2)$ mode).

In the range of the CH stretching vibrations, five strong lines appear due to the vibrations of the methylpyrrolidine moiety; the frequencies below 2800 cm^{-1} are due to the vibrations involving so-called Bohlmann hydrogen atoms that lie opposite to the lone pair of the nitrogen atom [14, 15].

CONCLUSIONS

The conformational composition of 2-thienyl-*N*-methylfulleropyrrolidine has been studied using experimental and computations methods. From the results of quantum-mechanical computations, the compound can exist as a mix of eight conformers with the energy differences between the conformers ranging from 2.4 to 31.4 kJ/mol and transition barriers between them ranging from 19.4 to 52.3 kJ/mol. The ^{1}H NMR spectrum of the compound in solution can correspond to either one conformer or an equilibrium mix of the two most stable species. The IR spectrum of the solid compound can be assigned in terms of the presence of one (the most stable) conformer with the methyl group in the equatorial position and the rotation angle of the thiophene moiety relative to the NCC angle equal to 39.8°. The full assignment of the spectrum has been carried out in terms of normal modes of the constituents of the diad (fullerene, thiophene, and *N*-methylpyrrolidine moieties).

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