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DFT B3LYP/6-311+G* calculation study of a new nonclassical mechanism of electrophilic functionalization of aromatic C─H bond *via* aryl cation formation

Yurii A. Borisov and Irena S. Akhrem

1. Computational details

Quantum-chemical calculations were carried out by DFT method using the Becke-Lee-Yang-Parr functional (B3LYP) with the 6-31G* basis set.[S1-S3] All calculations with full optimization of geometry were performed with the use of the program GAUSSIAN-09 under LINUX operating system.[S4] By calculating the normal vibration frequencies with the use of second derivatives, it was confirmed that the stationary points determined with geometry optimization were energy minima. The transition states (TSs) were calculated by quadratic synchronous transit methods QST2 and QST3[S5,S6] and were proved by the IRC method.[S7,S8] The Polarized Continuum model (PCM) was used for the calculation of solvent (CH_2Cl_2) effect of these reactions.[S9] The calculations of activation barriers and enthalpies for all reactions were calculated using B3LYP/ functional and 6-311+G* basis set[S3] involving the diffuse functions. Optimization of geometry for the calculation with diffuse functions was not performed. However, our calculations of the geometry of phenyl cation carried out by methods the DFT with B3LYP/6-31+G* and B3LYP/6-311+G* basis sets showed that both methods led to practically the same result (see Suppl. Data in Ref.[S10])..

2. Geometrical characteristics for adamantyl cation in their derivatives

Table S1. Geometrical characteristics for adamantyl cation in their derivatives.

Geometrical parameters [a]	1.3-$Ad_2C_6H_3$-5-Ad^+ Al_2Br_7(**4**) B3LYP/6-311+G* [this work]	1-Ad^+ B3LYP/6-311+G* [this work]	1-Ad^+ CCSD(T)/cc-pVTZ [Ref. S11]	1,3,5-$Me_3Ad_1^+$ $Sb_2F_{11}^-$ X-ray [Ref. S12]
Bond length in Å				
C(1)-C(2)	1.4694	1.4557	1.449	1.439
C(1)-C(2’)	1.4460	1.4557	1.449	1.439
C(1)-C(2’’)	1.4590	1.4557	1.449	1.439
C(2)-C(3)	1.6286	1.6282	1.610	1.612
C(2’)-C(3’)	1.6274	1.6282	1.610	1.612
C(2’’)-C(3’’)	1.6108	1.6282	1.610	1.612
Angle in °				
C(2)-C(1)-C(2’)	116.85	117.78	-	117.9
C(2’)-C(1)-C(2’’)	118.45	117.78	-	117.9
C(2’’)-C(1)-C(2)	118.26	117.78	-	117.9
Dihedral angle in °				
C(2)-C(1)-C(2’)-C(2’’)	151.47	150.93	-	151.47
C(2’)-C(1)-C(2’’)-C(2)	151.06	150.93	-	151.27
C(2’’)-C(1)-C(2)-C(2’)	151.52	150.93	-	151.27

[a]Atom numbering according to Figure **S1**

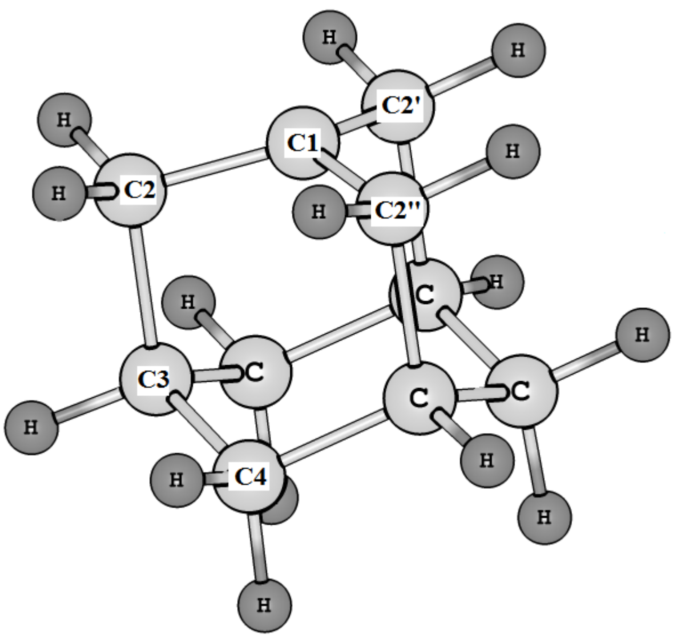

Figure S1 Structure of 1-Ad^+ (B3LYP/6-311+G*)

3. Geometrical parameters of acylium groups in 5 and crystal acylium salts

Table S2. Geometrical parameters of acylium groups in **5** and crystal acylium salts.

Acylium salt	Length of C^{+}=O bond in Å	Length of C(1)–C(2) in Å	Angle of CC=O in °	Reference
$Ad_2C_6H_3Ad_1CO^+$ $Al_2Br_7^-$ (**5**)	1.159	1.501	138.94	This work
CH_3CO^+ $SbCl_4^-$	1.109	1.452	180	[S13-S14]
CH_3CO^+ $AlCl_4^-$	1.11	1.45	179.8	[S13]
CH_3CO^+ SbF_6^-	1.108	1.385	177.2	[S15- S16]
o-$MeC_6H_4CO^+$ $SbCl_6^-$	1.111	1.387	178.7	[S 17]
p-$MeC_6H_4CO^+$ $SbCl_6$	1.097	1.396	179 [	[S18]

Table S3 Calculated geometrical parameters for 1-$AdCO^+$

Bond length, [a] Å Angle, °	DFT B3LYP/ 6-31G*	DFT B3LYP/ 6-311+G*	MP2/ 6-31G*	MP2/ 6-311+G*	MP3/ 6-311+G*
C=O	1.1338	1.1338	1.1468	1.1359	1.1124
C-C(1)	1.4189	1.4189	1.4279	1.4250	1.4443
C(1)-C(2)	1.5809	1.5809	1.5610	1.5612	1.5633
C(2)-C(3)	1.5447	1.5448	1.5360	1.5370	1.5426
C(3)-C(4)	1.5421	1.5418	1.5328	1.5343	1.5396
C(2)-H(2)	1.0950	1.0950	1.0965	1.0965	1.0955
C(3)-H(3)	1.0961	1.0961	1.0970	1.0968	1.0948
C(4)-H(4)	1.0976	1.0975	1.0963	1.0976	1.0952
OCC(1)	180.00	180.00	180.00	180.00	180.00
CC(1)C(2)	108.65	108.55	108.23	108.21	108.13
C(1)C(2)C(3)	107.02	106.99	106.86	106.89	106.94
C(1)C(2)H(2)	109.61	109.60	109.88	109.90	110.00
C(2)C(3)C(4)	109.90	109.86	109.76	109.70	109.61
C(2)C(3)H(3)	106.71	106.70	107.08	107.22	107.44
C(3)C(4)H(4)	110.58	110.55	109.70	110.60	110.64

[a] Atom numbering according to Figure S2

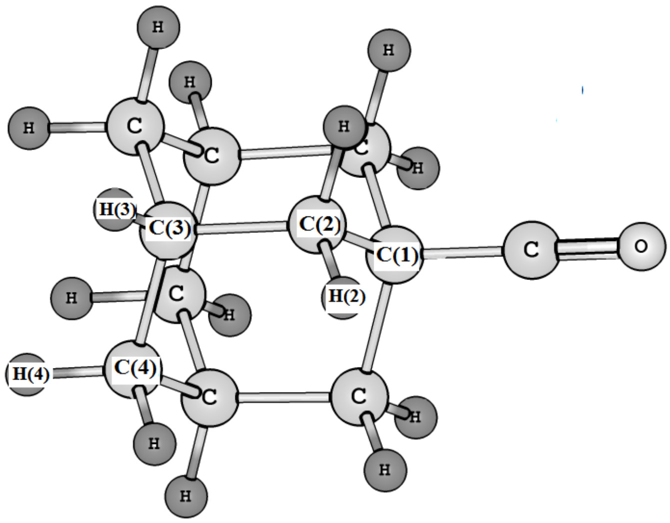

Figure S2. Structure of 1-AdCO+

4. Calculated geometrical parameters of acylium salts $RCO^+ AlCl_4$

Table S4 Calculated geometrical parameters of acylium salts $RCO^+ AlCl_4^-$

R (in RCO^+)	Angle CCO in Degrees		Bond length in Å C–C		Bond length in Å C–O		Distance in Å C----Hal	
	B3LYP/6-31G*	MP2/ 6-1G*	B3LYP/6 -31G*	MP2/ 6-1G*-	B3LYP/6-31G*	MP2/ 6-31G*-	B3LYP/6-31G*	MP2/ 6-31G*
$Ad_3C_6H_3$ **(5)****	(163.9)		(1,445)		(1.133)		(3.012)	
Ad	139.27 (172.03)	141.51		1.481 (1.426)		1.169 (1.134)		2.100 (3.299)
CH_3	136.67 (173.53)	137.16		1.482 (1.432)		1.172 (1.126)		2.038 (3.060)
Ad***	139.32 (172.03)	143.65		1.478 (1.426)		1.164 (1.134)		2.410 (3.299)

* Values in parentheses represent results of calculations with CH_2Cl_2 solvent effect. **The calculations for **5** in gas phase see in table 3. ***Ad*= $AdCO^+Al_2Br_7^-$

5. Calculated structures of acylium salts (MP2/ 6-31G*)

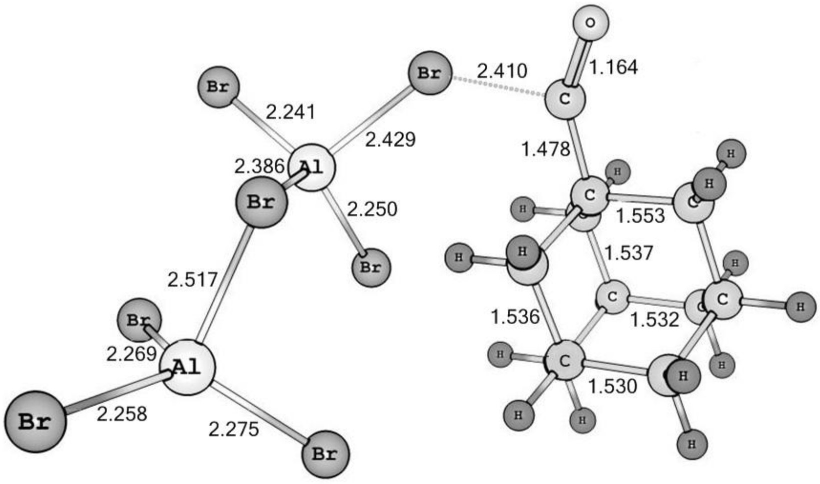

Figure S3. $AdCO^+ Al_2Br_7^-$

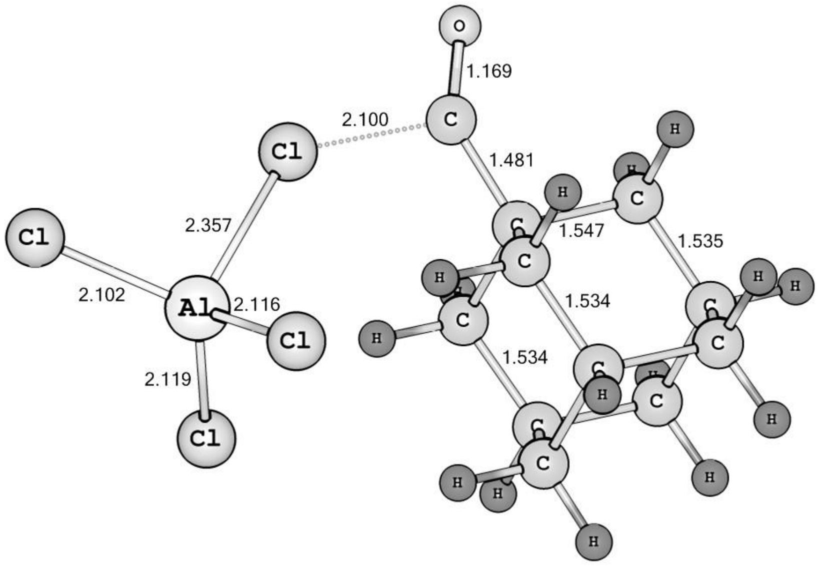

Figure S4. $AdCO^+ AlCl_4^-$

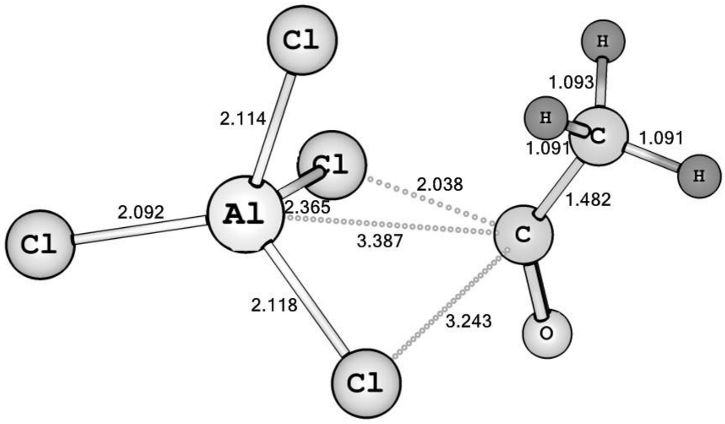

Figure S5. CH_3CO^+ $AlCl_4^-$

6 Calculation of the half-conversion time, $t_{1/2}$ for the reaction of $Ad_3C_6H_3$ / CBr_3^+ $Al_2Br_7^-$ / CO with the participation of aryl cation

Using the Erying equation S1 we have calculated the half-conversion time, $t_{1/2}$ (h) for the reaction of the second order (equation S2**)**.

$$K = \mu\ K_b\ T/h\ \exp \Delta G^{\ddagger}/RT \qquad \text{(equation S1)},$$

where μ is the transmission coefficient = 1; ΔG‡ = the free Gibbs energy of activation of the first stage at temperature T; h = the Planck constant; K_b = the Boltzmann constant ; T = absolute temperature in Kelvin.

$$t_{1/2} = (K\ C_0)\cdot 3600 \qquad \text{(equation S2)},$$

where: $t_{1/2}$ = the half-conversion time (h): C_0 = the initial concentration of $Ad_3C_6H_3$, that is equal to that of E.

The calculated $t_{1/2}$ at $C_{0\,=}$ 1 mole dm^{-3} are as follows: $t_{1/2}$ (h): 0.08 (365 °C); 0.11 (360 °C); 0.97 (320 °C); 3.26 (300 °C); 6.15 (290 °C); 11.88 (280 °C).

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