Electronic Supplementary Information for

Hydrogen Bond Induced Enhancement of Fermi Resonances in N–H···N Hydrogen Bonded Complexes of Anilines

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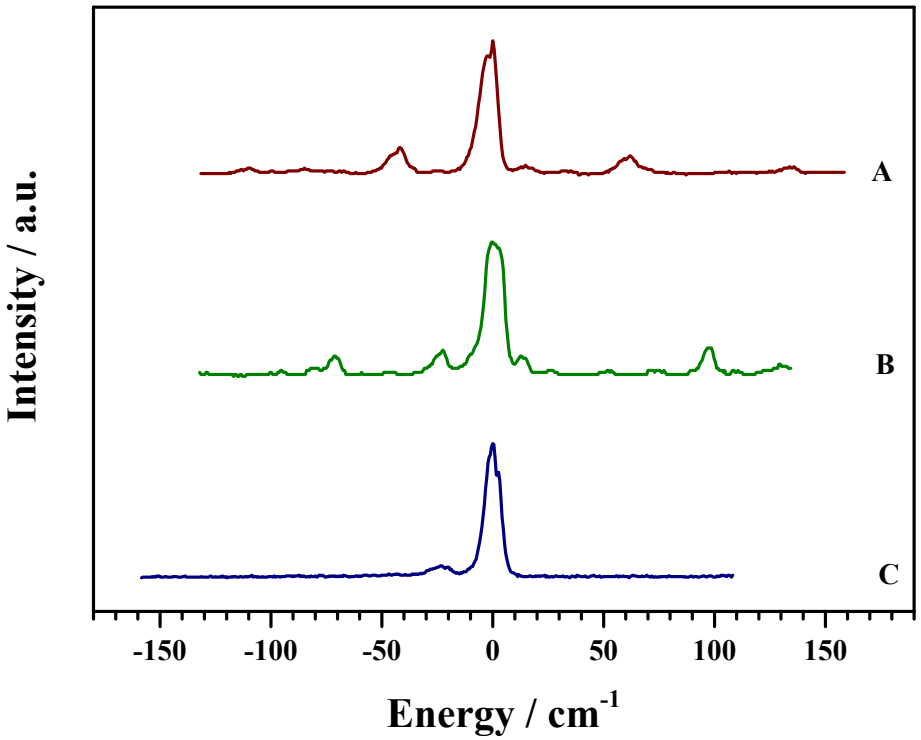

Figure S1. 1C-R2PI spectra of (A) aniline, (B) fluoroaniline and (C) ethynylaniline plotted relative to their band-origin transitions at 34032, 32635 and 32661 cm^{-1}, respectively.

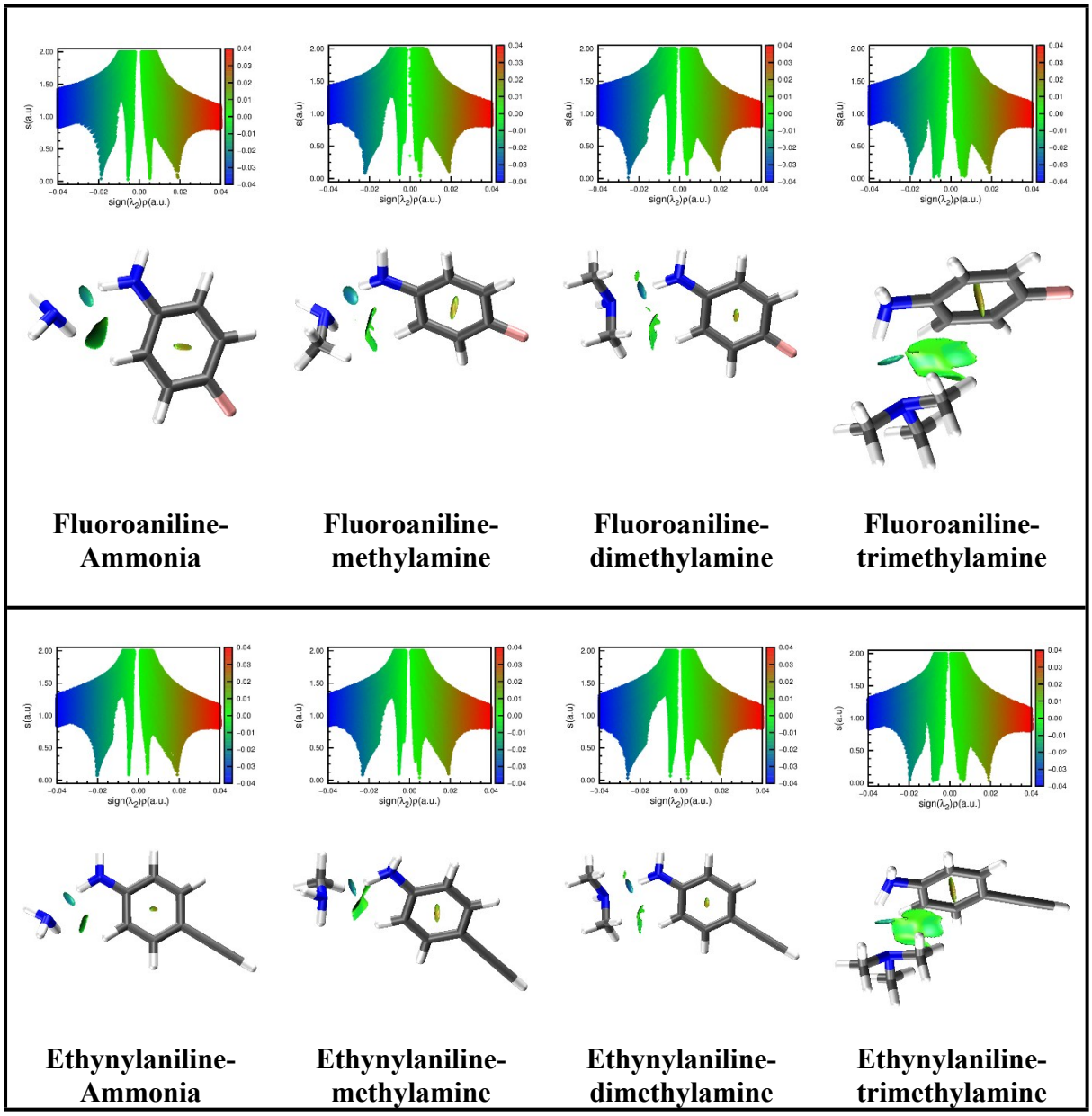

Figure S2. NCI isosurfaces and plots of reduced density gradient *s* against sign(λ_2)ρ for the complexes of fluoroaniline and ethynylaniline with ammonia, methylamine, dimethylamine and trimethylamine.

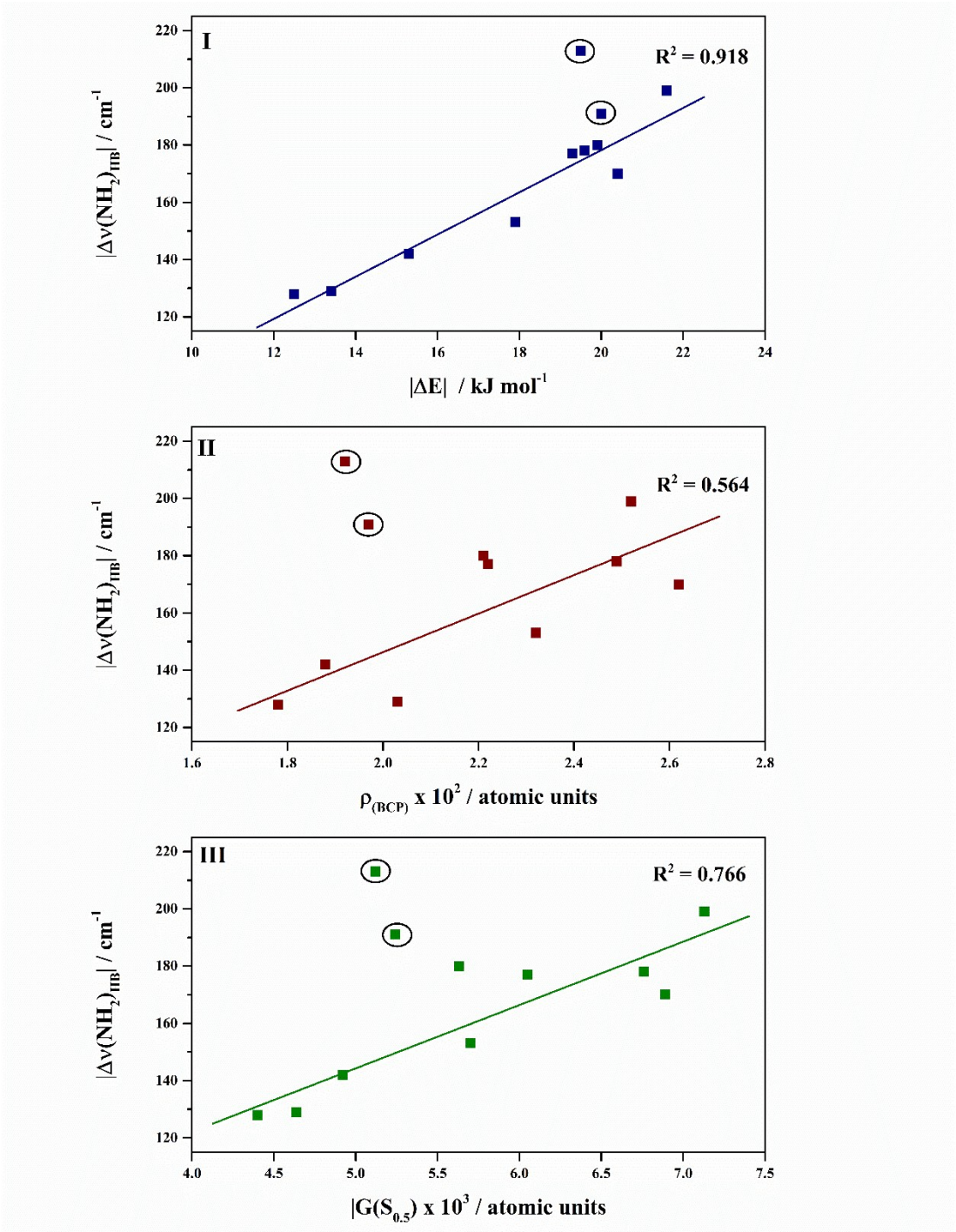

Figure S3. Correlation of estimated shifts in the zero-order hydrogen-bonded NH_2 stretching frequencies (see Table 2) against (panel-I) BSSE and ZPE corrected stabilization energies, (panel-II) electron density at the bond critical point and (panel-III) kinetic energy density integrated within the reduced density gradient volume with s = 0.5 a.u., $G(s_{0.5})$. The straight-line is a linear least-squares fit to the data points. The data points corresponding to trimethylamine complexes (circled) were omitted in the linear fit (see text).

Table S1: List of unscaled N–H stretching frequencies (cm^{-1}) and their intensities (km mol^{-1}) for aliphatic aminies, anilines and their complexes. Also given are acetylenic C–H stretching frequencies (in bold) for ethynylaniline and NH_2 bending vibrations (in italics) for anilines and their complexes.

Ammonia	3478 (5)	3633 (5)	3633 (5)	--	--	--	--	--
Methylamine	3512 (1)	3609 (3)	--	--	--	--	--	--
Dimethylamine	3536 (1)		--	--	--	--	--	--
Trimethylamine			--	--	--	--	--	--
Aniline	3546 (13)	3661 (16)	--	--	--	--	*1653 (122)*	*1632 (7)*
Fluoroaniline	3545 (13)	3659 (16)	--	--	--	--	*1657 (26)*	*1635 (15)*
Ethynylaniline	3549 (24)	3665 (18)	--	--	--	--	*1662 (122)*	*1634 (31)*
Aniline-Ammonia	3461 (60)	3468 (128)	3612 (10)	3622 (46)	3625 (9)	--	*1666 (58)*	*1622 (0.4)*
Aniline-Methylamine	3417 (361)	3502 (1)	3598 (4)	3630 (48)	--	--	*1673 (60)*	*1620 (0.4)*
Aniline-Dimethylamine	3378 (468)	3535 (2)	3616 (43)	--		--	*1675 (59)*	*1622 (1)*
Aniline-Trimethylamine	3433 (149)	3601 (37)	--	--	--	--	*1653 (70)*	*1622 (1.5)*
Fluoroaniline-Ammonia	3453 (200)	3467 (22)	3615 (9)	3620 (47)	3624 (9)	--	*1675 (90)*	*1642 (1.6)*
Fluoroaniline-Methylamine	3414 (352)	3502 (1)	3598 (5)	3626 (48)	--	--	*1677 (91)*	*1637 (5)*
Fluoroaniline-Dimethylamine	3372 (463)	3535 (3)	3614 (42)	--	--	--	*1679 (86)*	*1639 (3)*
Fluoroaniline-Trimethylamine	3430 (150)	3600 (37)	--	--	--	--	*1660 (81)*	*1642 (3)*
Ethynylaniline-Ammonia	3438 (408)	3470 (10)	**3483 (81)**	3619 (9)	3623 (8)	3634 (56)	*1667 (24)*	*1603 (0.7)*
Ethynylaniline-Methylamine	3401 (497)	**3483 (83)**	3502 (1)	3598 (4)	3634 (50)	--	*1674 (14)*	*1608 (1.6)*
Ethynylaniline-Dimethylamine	3356 (654)	**3483 (84)**	3535 (3)	3622 (43)	--	--	*1675 (31)*	*1603 (1.3)*
Ethynylaniline-Trimethylamine	3428 (187)	**3483 (85)**	3603 (40)	--	--	--	*1654 (12)*	*1604 (0.5)*

Coordinates of various monomers and N–H···N hydrogen bonded complexes calculated at MP2/aug-cc-pVDZ level of theory.

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Ammonia

N	0.00000000	0.00000000	0.11702000
H	0.00000000	0.94290200	-0.27304600
H	-0.81657700	-0.47145100	-0.27304600
H	0.81657700	-0.47145100	-0.27304600

Methylamine

N	-0.75434700	-0.00000500	-0.12585600
H	-1.15163800	0.81348400	0.34411300
H	-1.15169300	-0.81345800	0.34413700
C	0.71115400	-0.00000500	0.01842300
H	1.11901000	-0.88626100	-0.48950800
H	1.11894100	0.88631600	-0.48944800
H	1.07888600	-0.00001800	1.06116500

Dimethylamine

N	-0.00002000	0.58010500	-0.15408100
H	-0.00003900	1.32687800	0.54094900
C	-1.20990500	-0.22733300	0.02068500
H	-2.09933000	0.41666400	-0.04452400
H	-1.26564400	-0.96661800	-0.79425400
H	-1.24056200	-0.77994800	0.98346400
C	1.20991900	-0.22733700	0.02067500
H	1.26616400	-0.96611500	-0.79468300
H	2.09922100	0.41690200	-0.04371300
H	1.24024300	-0.78047900	0.98316900

Trimethylamine

N	0.00001400	0.00002200	-0.41162400
C	-1.18106300	0.71628300	0.06655200
H	-1.16445600	1.75086300	-0.30913500
H	-2.09079100	0.22334200	-0.30921800
H	-1.23274900	0.74751900	1.17949400
C	-0.02980600	-1.38094900	0.06655100
H	-0.93394500	-1.88390700	-0.30942300
H	0.85208900	-1.92227500	-0.30896800
H	-0.03136100	-1.44135000	1.17949700
C	1.21086600	0.66466700	0.06656000
H	2.09847400	0.13311200	-0.30944900
H	1.23871800	1.69908900	-0.30891400
H	1.26394300	0.69345000	1.17950600

Aniline

N	2.35303800	-0.00009000	-0.08692500

H	2.78351700	0.83419100	0.30319700
H	2.78358500	-0.83371800	0.30449800
C	0.94344000	-0.00004200	-0.00595100
C	0.22519600	-1.21588700	-0.00395700
C	0.22528400	1.21584200	-0.00389500
C	-1.18022500	-1.21331200	0.00346500
H	0.77156300	-2.16537500	-0.01417100
C	-1.18014700	1.21336100	0.00346400
H	0.77165700	2.16533300	-0.01400300
C	-1.89335700	0.00004500	0.00721800
H	-1.71813300	-2.16624000	0.00693300
H	-1.71797300	2.16633100	0.00696700
H	-2.98662900	0.00006700	0.01299600

Fluoroaniline

N	2.80281600	-0.00004100	-0.08603300
H	3.23016800	0.83243100	0.31161200
H	3.23017500	-0.83215600	0.31235400
C	1.39140200	-0.00000100	-0.00483500
C	0.67184000	-1.21475200	-0.00437500
C	0.67184400	1.21474800	-0.00433600
C	-0.73440400	-1.22264300	0.00005100
H	1.21403700	-2.16600500	-0.01411400
C	-0.73440400	1.22264400	0.00004600
H	1.21403500	2.16600600	-0.01399700
C	-1.41156000	0.00000300	0.00219100
H	-1.29693000	-2.15926100	0.00225100
H	-1.29692700	2.15926500	0.00225700
F	-2.78250900	0.00000200	0.00771300

Ethynylaniline

C	1.03324100	-1.21421900	-0.00452900
C	-0.36848300	-1.21674600	-0.00190000
C	-1.09065700	0.00000500	-0.00006100
C	-0.36848200	1.21673300	-0.00191500
C	1.03326200	1.21418600	-0.00438200
C	1.75481700	-0.00001500	-0.00375100
H	1.57670600	-2.16524300	-0.01264900
H	-0.91401500	-2.16463100	0.00002600
H	-0.91399700	2.16462800	0.00007400
H	1.57667400	2.16524800	-0.01220300
C	-2.52872000	0.00001100	0.00388300
C	-3.76579600	0.00001800	0.00770700
H	-4.83979800	0.00001300	0.00945700
N	3.16091400	-0.00014000	-0.07945100
H	3.59640500	0.83650000	0.29909900
H	3.59653300	-0.83537300	0.30203800

Aniline-ammonia

N	-1.27835100	-1.43321500	-0.62718200
H	-1.30027600	-2.33616400	-0.16004500
H	-2.14268700	-0.91463700	-0.45019900
C	-0.13383900	-0.67739800	-0.31267100
C	-0.08587900	0.69677300	-0.64888300
C	1.00686900	-1.26602200	0.27980500
C	1.06325400	1.46051900	-0.38031600
H	-0.94889100	1.15184300	-1.14531100
C	2.15958000	-0.50193400	0.53281000
H	0.98925400	-2.33033200	0.53994800
C	2.19452600	0.86837300	0.21301400
H	1.07798600	2.52137300	-0.64958900
H	3.03089400	-0.98049000	0.99070400
H	3.09010400	1.46221700	0.41505900
N	-3.19042900	0.70823300	0.60066400
H	-2.32331400	1.01977400	1.04272500
H	-3.83175600	0.47020000	1.35776100
H	-3.58691700	1.52922800	0.14202100

Aniline-methylamine

N	-0.72159600	-1.46484400	0.04372700
H	-0.57826300	-2.41168700	0.38205800
H	-1.54722000	-1.02288100	0.46094600
C	0.43480100	-0.67022100	0.06195400
C	0.33801500	0.73812000	0.15993800
C	1.71777200	-1.24661400	-0.08723900
C	1.48888500	1.54303800	0.10354900
H	-0.64778600	1.19514600	0.28689600
C	2.86641700	-0.43895400	-0.13696900
H	1.80994100	-2.33525900	-0.17032200
C	2.76226300	0.96228600	-0.04542600
H	1.38799600	2.63007200	0.18273900
H	3.84809000	-0.90938900	-0.25079800
H	3.65711900	1.58919900	-0.08698900
N	-3.23602100	0.18837800	0.65996000
H	-3.10369300	1.07430600	1.14937900
H	-4.09254400	-0.21140600	1.04369300
C	-3.40182700	0.43067000	-0.78875800
H	-2.46261000	0.83605200	-1.19275900
H	-3.58266900	-0.53131200	-1.28854600
H	-4.22300200	1.12246700	-1.04439300

Aniline-dimethylamine

N	-0.40921700	-1.23611800	-0.10457800
H	-0.38521300	-2.20919100	0.18772500
H	-1.18272900	-0.72411400	0.33723000
C	0.83571000	-0.59133100	-0.01109500

C	0.90147300	0.81594400	0.11578900
C	2.04508500	-1.31694400	-0.10971800
C	2.14201300	1.47572000	0.14141700
H	-0.02893600	1.38648200	0.19159500
C	3.28368400	-0.65341400	-0.08168400
H	2.01031200	-2.40718300	-0.21395700
C	3.34288700	0.74769300	0.04313700
H	2.16831700	2.56526400	0.24257300
H	4.20665000	-1.23671700	-0.15810300
H	4.30739800	1.26232900	0.06414200
N	-2.93779700	0.28216200	0.51705600
H	-3.36907600	0.67642400	1.35302400
C	-3.76798000	-0.82539100	0.02454400
H	-3.24421400	-1.30846600	-0.81572300
H	-3.90421600	-1.57066100	0.82243400
H	-4.76513800	-0.49943200	-0.33261200
C	-2.80375100	1.33457100	-0.49884100
H	-2.28259200	2.20263700	-0.06878200
H	-2.19844400	0.94560700	-1.33332300
H	-3.77775000	1.67361900	-0.90486700

Aniline-trimethylamine

N	-0.03026500	1.78367500	-1.06854700
H	-0.03206400	2.65811200	-0.54711600
H	0.90174300	1.35620800	-1.03224000
C	-0.97739600	0.86101300	-0.57291400
C	-0.96049900	-0.46412900	-1.06536200
C	-1.95552900	1.21887800	0.38027500
C	-1.87134600	-1.41769400	-0.58067500
H	-0.22544300	-0.73335800	-1.82986400
C	-2.87967400	0.26708700	0.84931300
H	-1.98356000	2.24435000	0.76594000
C	-2.83473300	-1.06055800	0.38374300
H	-1.83711600	-2.44146800	-0.96693100
H	-3.62738300	0.56274000	1.59179800
H	-3.54699500	-1.80181500	0.75663400
N	2.09987100	-0.12791100	0.07867800
C	2.30384700	-1.52546800	-0.30964000
H	1.33133900	-2.03845800	-0.34717100
H	2.76878800	-1.57019900	-1.30698100
H	2.96010400	-2.06538700	0.40936300
C	3.39183300	0.55755600	0.15858900
H	3.88934000	0.52680300	-0.82322100
H	3.23504200	1.61083700	0.44071300
H	4.06800000	0.09261200	0.91051400
C	1.42798400	-0.07443700	1.38155500
H	1.23778700	0.97496900	1.65644300
H	0.46202400	-0.59739500	1.32062900
H	2.04422500	-0.54239000	2.18126100

Fluoroaniline ammonia

N	1.94372400	1.31346500	-0.52920000
H	2.09779900	2.18834000	-0.03437400
H	2.69113800	0.64554900	-0.31949400
C	0.66732400	0.76629600	-0.29198900
C	0.39609400	-0.57040100	-0.66916100
C	-0.38405500	1.53508200	0.25716300
C	-0.88054600	-1.13214100	-0.48790900
H	1.19013000	-1.16442200	-1.13135200
C	-1.67013800	0.99148600	0.43069100
H	-0.19771800	2.57376300	0.55020100
C	-1.89170800	-0.33763700	0.06043300
H	-1.09496900	-2.16311500	-0.78014100
H	-2.48522700	1.58407600	0.85325300
N	3.49145600	-1.15054200	0.60000700
H	2.62922900	-1.41525200	1.07976100
H	4.20056600	-1.03843600	1.32509500
H	3.77433400	-1.96423800	0.05277300
F	-3.14148500	-0.87809300	0.23480600

Fluouoaniline methylamine

N	-1.32617900	1.49959300	-0.03101800
H	-1.30268300	2.45072400	-0.38735200
H	-2.08819600	0.95478000	-0.44843300
C	-0.07822100	0.85260800	-0.06477800
C	-0.00087900	-0.55507100	-0.18114800
C	1.12466700	1.57967600	0.08980200
C	1.23668300	-1.22245300	-0.13847500
H	-0.92160100	-1.12983600	-0.31321500
C	2.36970500	0.92716500	0.12656100
H	1.08589000	2.66953400	0.18906800
C	2.40137000	-0.46593100	0.01517800
H	1.30007900	-2.30961800	-0.22921300
H	3.30083500	1.48701400	0.24367700
N	-3.61446500	-0.45373900	-0.65094400
H	-3.41388600	-1.31892600	-1.15406400
H	-4.50706900	-0.12443500	-1.01924300
C	-3.74179600	-0.72814000	0.79610000
H	-2.76759400	-1.06013800	1.18409000
H	-3.99505300	0.20878900	1.31164700
H	-4.49943400	-1.48909700	1.05087400
F	3.61378300	-1.10965600	0.05405100

Fluoroaniline-dimethylamine

N	-0.95130700	1.30670200	0.11823400
H	-1.00264700	2.27207700	-0.19616100
H	-1.67667400	0.72946100	-0.32582200
C	0.34232600	0.75988500	0.02327200
C	0.51750700	-0.63819300	-0.09734000
C	1.49224800	1.57638400	0.11713500
C	1.80221000	-1.20976600	-0.12269600
H	-0.36369500	-1.28154900	-0.16953400
C	2.78338200	1.01912800	0.09085900
H	1.37719700	2.66079400	0.21779300

C	2.91341900	-0.36745700	-0.02785000
H	1.94235900	-2.28935000	-0.21765000
H	3.67468300	1.64736600	0.16175200
N	-3.32624600	-0.43262700	-0.51973100
H	-3.70531700	-0.87439200	-1.35729600
C	-3.12676800	-1.45475500	0.51633900
H	-2.52834500	-2.28407900	0.11093600
H	-2.57250800	-1.00452000	1.35551400
H	-4.07748000	-1.86656100	0.90973100
C	-4.25752300	0.60813600	-0.06271000
H	-3.79547300	1.14553000	0.78077300
H	-4.43785500	1.32771600	-0.87525900
H	-5.23137400	0.20415500	0.27820500
F	4.17102200	-0.91837200	-0.05383900

Fluoroaniline -trimethylamine

N	0.65136800	2.02710200	-0.86488900
H	0.73987600	2.82495800	-0.23861300
H	1.50662700	1.46091400	-0.82803200
C	-0.44811900	1.20343100	-0.52821100
C	-0.60782500	-0.02623700	-1.20660700
C	-1.40266500	1.56933100	0.44511500
C	-1.66779700	-0.89407300	-0.89154900
H	0.10996200	-0.29793400	-1.98571800
C	-2.48279400	0.72122000	0.75636200
H	-1.29664300	2.52030400	0.97816100
C	-2.58509400	-0.50297000	0.08994100
H	-1.79551000	-1.84978100	-1.40633200
H	-3.22429100	0.99567100	1.51064100
N	2.37413100	-0.33402500	0.10211400
C	2.40401000	-1.67833700	-0.47928800
H	1.37356800	-2.03284600	-0.63093200
H	2.91799800	-1.65098000	-1.45284700
H	2.93280000	-2.40440000	0.17793900
C	3.74247800	0.13535200	0.33406900
H	4.28960200	0.16938100	-0.62083100
H	3.71801800	1.15017200	0.76201700
H	4.29941100	-0.52499700	1.03557400
C	1.63877100	-0.36476400	1.37098200
H	1.57812900	0.65290600	1.78777300
H	0.61564100	-0.72965200	1.19640300
H	2.13477500	-1.02315800	2.11823700
F	-3.62491700	-1.34331200	0.39901100

Ethynylaniline-ammonia

C	0.64815600	-0.59201500	-0.42686400
C	-0.68528800	-1.01335800	-0.33569100
C	-1.71037100	-0.09648300	-0.00145100
C	-1.35783600	1.25325100	0.23611200
C	-0.02207000	1.66882000	0.14795500
C	1.00633600	0.75571900	-0.18289400
H	1.42867200	-1.30727400	-0.70424300

H	-0.94381100	-2.05887900	-0.52768500
H	-2.13916800	1.97386700	0.49455300
H	0.23059600	2.71835900	0.33510200
C	-3.07929300	-0.52658900	0.09146700
C	-4.25717600	-0.89697400	0.17322000
H	-5.27994000	-1.21719600	0.24139300
N	2.33425900	1.16993500	-0.33527500
H	2.55227500	2.04893200	0.12443200
H	3.02651800	0.44276800	-0.13285200
N	4.10407600	-1.30892400	0.39537400
H	3.52385800	-1.81190200	1.06835700
H	5.00929000	-1.17525900	0.84686200
H	4.26862900	-1.95471700	-0.37773800

Ethynylaniline-methylamine

C	0.65341100	1.77190600	-0.08829000
C	1.95062000	1.24231500	-0.10913400
C	2.16235400	-0.15280400	0.00111000
C	1.03568700	-0.99796900	0.13748000
C	-0.25942800	-0.46270800	0.16166800
C	-0.47661800	0.93140300	0.04740600
H	0.50929000	2.85374700	-0.18330200
H	2.81192900	1.90858300	-0.21286100
H	1.18415500	-2.07788600	0.22932000
H	-1.12089300	-1.12698900	0.27623600
C	3.49204700	-0.69944300	-0.02187700
C	4.63660300	-1.16943000	-0.04098700
H	5.63005800	-1.57670000	-0.05889800
N	-1.77528000	1.44772700	0.00154900
H	-2.49654000	0.84311900	0.40987500
H	-1.85554800	2.41590200	0.29641400
C	-3.99238500	-1.02757400	-0.77418200
H	-4.36944300	-0.15063000	-1.31887700
H	-4.65684200	-1.88436100	-0.97972600
H	-2.99336200	-1.25548200	-1.17394600
N	-3.86948100	-0.68005900	0.65740600
H	-4.78719100	-0.44377600	1.03524400
H	-3.55602900	-1.49338000	1.18867100

Ethynylaniline-dimethylamine

N	-0.40933400	-1.23610100	-0.10421900
H	-0.38536700	-2.20918400	0.18804000
H	-1.18280400	-0.72406300	0.33761200
C	0.83560800	-0.59135200	-0.01088900
C	0.90142100	0.81588900	0.11628000
C	2.04496200	-1.31693400	-0.10995100
C	2.14195000	1.47566700	0.14173500
H	-0.02897500	1.38640000	0.19246100
C	3.28356500	-0.65341000	-0.08206700
H	2.01017300	-2.40714900	-0.21442900
C	3.34280500	0.74766400	0.04302800

H	2.16828200	2.56518800	0.24311500
H	4.20650900	-1.23670300	-0.15882300
N	-2.93775200	0.28246200	0.51694300
H	-3.36928000	0.67713800	1.35258800
C	-2.80342500	1.33435800	-0.49946500
H	-2.28249000	2.20267400	-0.06964900
H	-2.19778500	0.94499100	-1.33351900
H	-3.77730800	1.67311800	-0.90599700
C	-3.76783100	-0.82533300	0.02476000
H	-3.24391500	-1.30870800	-0.81524000
H	-3.90414000	-1.57027000	0.82294500
H	-4.76494300	-0.49954800	-0.33266900
C	4.70124740	1.47248783	0.07243306
C	5.76083248	2.03785042	0.09536900
H	6.70468531	2.54146178	0.11579979

Ethynylaniline-trimethylamine

N	-0.03026500	1.78367500	-1.06854700
H	-0.03206400	2.65811200	-0.54711600
H	0.90174300	1.35620800	-1.03224000
C	-0.97739600	0.86101300	-0.57291400
C	-0.96049900	-0.46412900	-1.06536200
C	-1.95552900	1.21887800	0.38027500
C	-1.87134600	-1.41769400	-0.58067500
H	-0.22544300	-0.73335800	-1.82986400
C	-2.87967400	0.26708700	0.84931300
H	-1.98356000	2.24435000	0.76594000
C	-2.83473300	-1.06055800	0.38374300
H	-1.83711600	-2.44146800	-0.96693100
H	-3.62738300	0.56274000	1.59179800
H	-3.54699500	-1.80181500	0.75663400
N	2.09987100	-0.12791100	0.07867800
C	2.30384700	-1.52546800	-0.30964000
H	1.33133900	-2.03845800	-0.34717100
H	2.76878800	-1.57019900	-1.30698100
H	2.96010400	-2.06538700	0.40936300
C	3.39183300	0.55755600	0.15858900
H	3.88934000	0.52680300	-0.82322100
H	3.23504200	1.61083700	0.44071300
H	4.06800000	0.09261200	0.91051400
C	1.42798400	-0.07443700	1.38155500
H	1.23778700	0.97496900	1.65644300
H	0.46202400	-0.59739500	1.32062900
H	2.04422500	-0.54239000	2.18126100